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Chain organization and photophysics of conjugated polymer in poor solvents: Aggregates, agglomerates and collapsed coils

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Abstract

UV/vis absorption, excitation, and emission spectroscopies are utilized to explore the association behavior of conjugated polymer, poly-[2-methoxy, 5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV), in a homologous series of linear alcohols and solvent–nonsolvent systems. We demonstrate that the aggregation, agglomeration, and collapse of isolated chains, which all take place in the poor solvents, exhibit different optical signatures. The aggregate, in which chromophores interact electronically, causes a red shift of absorption and emission spectra while the weak interaction of chromophores in the agglomerates leaves electronic properties unaltered. The collapse of isolated chain is accompanied by a blue shift of the spectra. Energy transfer from excited chromophores of non-aggregated chains to the lower energy aggregates is significantly diminished in the system of alcohol solvents, allowing separate emissions from various chromophores to occur. The optical signatures and extent of energy transfer are used as tools to elucidate the association mechanism and chain organization of isolated chains into large particles upon decreasing solvent quality. The extreme collapse of isolated chains in the very poor solvents is found to inhibit the chain organization into aggregates.

Keywords: MEH-PPV; Molecular assembling; Energy transfer

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1. Introduction

Conjugated polymers have gained tremendous interest recently due to their unique optical and electrical properties [1–5]. One of the most promising areas of conjugated polymers is for flat panel display application, known as organic light emitting diode (OLED) [1,2]. The fabrication process of this device involves casting polymeric solution into thin film. Conjugated chains in solid state tend to form aggregates, driven mainly by favorable local π–π interaction and their rigid-rod nature [6–9]. The aggregation in this sense refers to the association of multiple conjugated backbones that results in photophysical change of the chromophores [10]. Therefore, the aggregation requires that extent of interchain stacking has to be significant enough to allow the delocalization of π-electrons from one conjugated system to their neighboring chains. Theoretical studies suggest that interchain distance of the stacked chains required for altering the electronic properties of individual chains is about 3.5–4 Å [11,12]. Other types of interchain association where chromophores do not interact electronically are called agglomeration as suggested in literature [10].

The aggregation of conjugated polymers is one very important phenomenon because the chains in aggregated state exhibit electronic properties distinct from that of the isolated chains. The aggregation has been known to cause a red-shift peak in absorption and emission spectra [13–25]. However, the restriction of phenyl ring rotation due to the increased

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confinement within aggregates [26,27] and the collapse of isolated chains [28,29] are also suggested to be other factors responsible for the red shift. The aggregation reduces luminescence efficiency [10,18–20,23], posting a major problem for the development of conjugated polymers as a material for OLED application. One can reduce the magnitude of aggregation, at least to some extent, by incorporating bulky side groups into the conjugated backbone [14,30–34].

Studies have shown that local arrangement of conjugated polymers in solution affects optical properties of the prepared films [10,35,36]. In addition, an ability to control the polymer association in solutions allows one to grow various types of nanostructures on the surface of solid substrates [37]. Therefore, it is rather important to understand factors that dictate the properties of conjugated chains in solution. In this contribution, we investigate the association behavior of the well-known conjugated polymer, poly[2-methoxy, 5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) (see chemical structure in Fig. 1a). The polymer is constituted of an aromatic backbone and asymmetric alkoxy side chains, making it virtually a nonpolar molecule. The MEH-PPV can dissolve to relatively high quantity in both non-aromatic and aromatic solvents including chloroform, dichloromethane, toluene, *p*-xylene, and pyridine. The isolated chains dispersed in these solvents can be induced to form aggregates by addition of a poor solvent [17,20] or by increasing concentration [36].

Most of the earlier studies mainly focus on investigating the electronic properties of the aggregated chains. Details of the aggregation process, however, are usually overlooked. In addition, the controversies over the origins of the red-shift peak detected in the absorption and emission spectra upon decreasing solvent quality still remain [26–29]. This study explores the

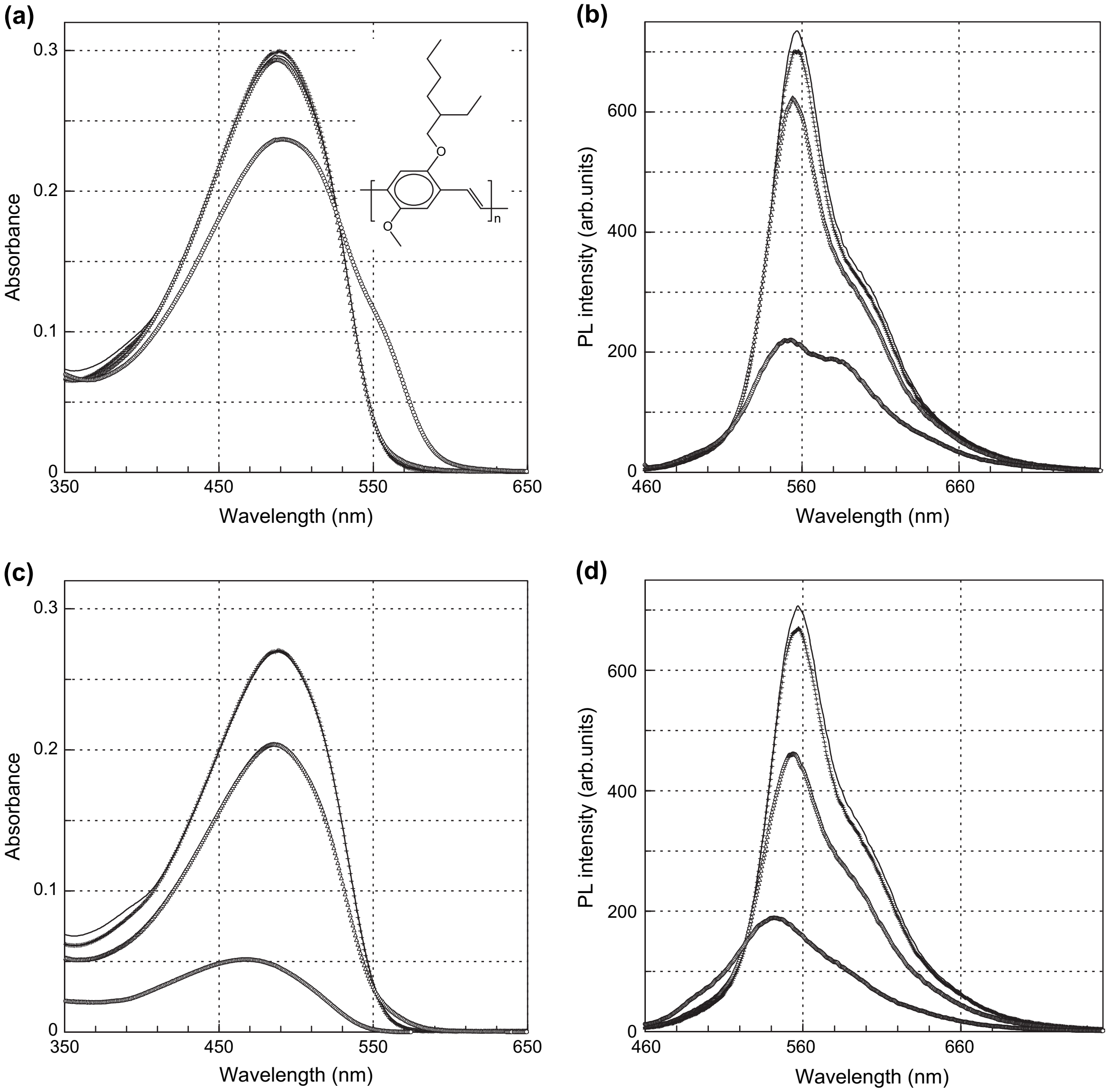

Fig. 1. (a,c) UV/vis absorption and (b,d) photoluminescence (PL) spectra of 0.01 mg/mL MEH-PPV (chemical structure shown as inset) in various mixtures of solvents measured before (a,b) and after (c,d) filtration by nylon membrane with 0.45 μm pore size. For PL spectra, excitation wavelength of 450 nm was used. Solvents: (–) pure chloroform, (+) chloroform + (20% v/v) hexanol, (△) chloroform + (60% v/v) hexanol, (○) chloroform + (80% v/v) hexanol.

association mechanism of the MEH-PPV in various mixtures of solvents and a homologous series of linear alkyl alcohols. Optical signatures of the aggregation, the agglomeration, and the collapse of isolated chains are distinguished. The effects of solvent quality on chain organization into aggregates and energy transfer between different chromophores are addressed. The selection of the alcohols as solvents provides simultaneous systematic change in solvent architecture and polarity.

2. Experimental section

MEH-PPV was synthesized according to the procedure described in literature [38]. The molecular weight (M_n) determined by GPC using polystyrene standard is 66,000 g/mol with polydispersity (M_w/M_n) of 4.2. Fresh solutions were prepared by dissolving the powder of the polymer in chloroform (AR Grade). The samples were diluted from the same stock solution by using various ratios of chloroform and alcohols. Another set of solutions was prepared by dissolving the polymer directly into pure alcohols. Although the MEH-PPV is normally difficult to dissolve in poor solvents like methanol and ethanol, its relatively small molecular weight and a sonication for several hours allow polymers to be dispersed in solution. The stock solutions were then diluted to the concentrations where colloidal particles were not visually observed. All solutions appeared homogeneous. Since the solutions were not filtered, same distribution of molecular weights was preserved in all samples. Absorption spectra were recorded on Analytica Specord 100 UV/vis spectrometer using a 1 cm thick quartz cuvette. Measurements of emission and excitation spectra were carried out on Perkin–Elmer LS55. To minimize the self-absorption effects, a 1 mm thick quartz cuvette was used, allowing the detection of photon emission from front surface.

3. Results and discussion

3.1. Photophysics of isolated chains, agglomerates and aggregates

Isolated chains of MEH-PPV dissolved in a good solvent, chloroform, exhibit a broad absorption spectrum with λ_{max} at ~495 nm as shown in Fig. 1a. Its emission pattern consists of a sharp peak at 558 nm with shoulder near 590 nm (Fig. 1b), corresponding to the relaxation of excited π-electrons to different vibrational energy levels of electronic ground state. These characteristics of the absorption and emission spectra arise from an intrinsic nature of chromophores of the conjugated chains. Although conjugated backbone is a rather rigid one, the chain can adopt various conformations [39–43]. The twisting of main chain randomly introduces physical defects along conjugated backbone, preventing the delocalization of π-electrons throughout the entire polymeric molecule [10,41]. Therefore, isolated chain of MEH-PPV can be considered as an ensemble of quasi-localized chromophores with various conjugation lengths where its averaged value is about 10 repeat units [43,44]. However, the true number varies with local conformation of conjugated backbone [43]. Comprehensive works by Schwartz's group [10,36,45] and our recent study [17] have demonstrated that conjugation length of PPV decreases significantly when the relatively extended chain [39,40] in good solvents is forced to collapse in poor solvent. These individual chromophores, connected via the physical [10,17,41] or chemical defects [29,46], absorb light at different wavelengths yielding a broad absorption band. The emission pattern, however, reflects the electronic properties of those chromophores with lowest transition HOMO–LUMO energy gap. It has been shown that efficient energy transfer from the shorter conjugation length segments to the nearby longer conjugated segments takes place prior to the emission process [41,42,46].

Addition of relatively small quantity of hexanol (20 and 60% v/v) into a solution of MEH-PPV in chloroform hardly affects the absorption pattern. Although same amount of photons is absorbed at 450 nm (i.e. same absorbance), the emission intensity recorded by using excitation energy at this wavelength gradually decreases upon increasing ratio of the poor solvent. This suggests the existence of additional nonradiative pathways for the excited chromophores. Further increasing the volume fraction of hexanol to 80% leads to the growth of a broad absorption band near 550 nm while the absorbance at ~490 nm simultaneously decreases (see Fig. 1a). Its emission spectrum in Fig. 1b changes accordingly. The overall intensity drastically drops while the ratio of peak intensity at 590/558 nm increases. The ratios of absorbance at 550/490 nm and emission intensity at 590/558 nm as a function of hexanol volume fraction are illustrated in Fig. 2a. Our results are consistent with other solvent–nonsolvent systems reported in literatures [13–17,19–22,24,25,37]. Series of studies performed on PPVs and its oligomers by Rothberg's group indicate the existence of two distinct electronic species, well packed and isolated chains, in the system [19,20,47]. The studies of phenylenevinylene oligomers also rule out the effects of chain folding onto itself upon decreasing solvent quality. Furthermore, the absorption and emission spectra of isolated chain in collapsed coil conformation do not show the red-shift characteristics [10,17,45]. The filtration experiment carried out by Bunz's group [25] on dialkyl-polyphenyleneethynylenes (PPE) is consistent with the two-species model. Kim and Swager demonstrate the relationship between different types of chain packing and photophysical changes by utilizing Langmuir films of various surfactant PPEs [48]. By forcing the conjugated chains to arrange in cofacial fashion, distinct red-shift peak in absorption and emission spectra is observed. Therefore, the red-shift shoulder in absorption pattern, the increase of emission intensity ratio at 590/558 nm as well as the drop of emission efficiency in our system are optical signatures of the interchain aggregation, induced by the decrease of polymer solubility and a favorable π–π interaction of the conjugated backbones.

To further explore the nature of interchain association in these solvents, we carried out filtration experiments. All solutions were passed through a nylon membrane with averaged pore size of 0.45 μm. Absorption and emission spectra of

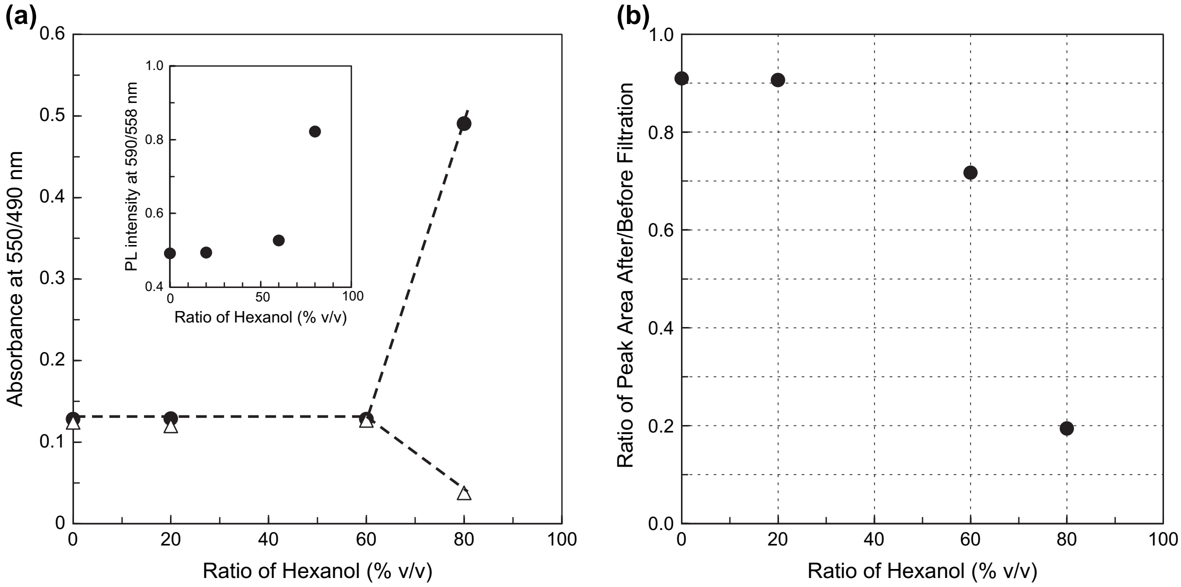

Fig. 2. (a) Variation of ratios of absorbance at 550/490 nm of 0.01 mg/mL MEH-PPV solutions in mixtures of chloroform and hexanol. Symbols: (●) before and (△) after the filtration. Dashed lines are for guiding. Inset shows the variation of ratios of PL intensity at 590/558 nm of the unfiltered solutions. (b) Ratios of integrated area of absorption band (650–350 nm) after/before filtration as a function of hexanol volume fraction.

the filtered solutions are illustrated in Fig. 1c and d, respectively. It has been reported that the averaged hydrodynamic radius of isolated MEH-PPV chain, depending on local polymer–solvent interactions and molecular weight, ranges from 10 to 40 nm [10,36,40,43], a much smaller dimension compared to the pore size of membrane. The hydrodynamic radius of the polymer in this study is expected to be smaller than this range because of its lower molecular weight. The filtration of isolated chains in pure chloroform causes slight decrease of absorbance and emission intensity. The integrated area of absorption band of filtered solution relative to that of the unfiltered one (see Fig. 2b) detects ~10% decrease of polymer concentration. Filtration of the polymer solution in mixture of chloroform and 20% v/v hexanol shows the same result. These results indicate that most of the isolated chain can pass through the filter as expected. The 10% drop of concentration after the filtration is attributed to adsorption by the membrane. Shape of absorption spectra of the filtered solution appears unchanged. This is illustrated in Fig. 2a where the ratio of absorbance at 550/490 nm remains the same.

Filtration of MEH-PPV solution in mixture of chloroform and 60% v/v hexanol shows rather different result. The drop of absorbance and emission intensity after the filtration is higher compared to the solution in pure chloroform. The relative integrated area of absorption band of filtered solution (see Fig. 2b) shows 30% drop of polymer concentration. This indicates that about 20% of MEH-PPV associates into large particles with overall diameter larger than the pore size of membrane (0.45 μm). The effect of this type of interchain association on electronic properties of chromophore is minimal. Its absorption and emission spectra almost superimpose those of the isolated chains in chloroform. The decrease of emission intensity, probably due to interchain quenching, is a major result of this type of association. Slight blue shift of the emission spectrum is attributed to the change of local structure as will be discussed in the following section. Throughout the later discussion, we refer to the association that does not lead to photophysical change of chromophores (i.e. red shift) as an agglomeration. To confirm our finding, another series of experiments were carried out by using pyridine in place of chloroform. Same results were observed where the agglomeration occurred prior to the aggregation.

The filtration of polymer solution in mixture of chloroform and 80% v/v hexanol causes the absorption band at 550 nm, proportional to aggregate concentration, to vanish. The absorption band of agglomerates center at ~490 nm also decreases significantly. The relative integrated area of absorption band of filtered solution detects ~80% drop of polymer concentration (see Fig. 2b). In this unfavorable local environment, large fraction of the MEH-PPV assembles into large particles to minimize interfacial contact. The assembling process upon addition of poor solvent is expected to take place at relatively fast rate and occur in a random fashion, preventing the chains to organize. Therefore, most of the polymeric chain forms agglomerates. The presence of large fraction of agglomerates is inferred from a significant drop of absorption band at ~490 nm after the filtration. This type of unorganized packing is consistent with its solid state structure, in which most of the chain exists in amorphous form [7,9]. The unorganized arrangement does not allow the π-orbitals of different conjugated backbones to overlap, leaving electronic properties of the chromophores unaltered. However, some segments of conjugated backbone or chromophores can stack efficiently (i.e. aggregate), which results in a red shift of absorption and emission spectra [11,12]. The aggregated sites are expected to distribute randomly within the large polymeric particles. Our argument is parallel to the proposed chain organization of PPV in thin films where different types of molecular packing cause the variation in emission dynamics [33]. In their system, magnitude of the interchain stacking is systematically controlled by incorporating various amounts of bulky side chains into conjugated backbone. Absorption and emission spectra of the filtered solution shift to relatively high-energy region. The shape of emission spectra also changes significantly. The discussion of this issue is postponed to later discussion.

Varying polymer concentration affects the extent of interchain aggregation. Fig. 3 illustrates the absorption and emission spectra of MEH-PPV in mixture of chloroform and 80% v/v hexanol measured from a series of polymer concentrations ranging from 0.001 to 0.05 mg/mL. The detection of red-shift peak in absorption and emission spectra accompanied with results from filtration experiments indicates the existence of aggregates and agglomerates in all solutions. However, the fraction of aggregates varies significantly with concentration. The increase of absorbance ratios at 550/490 nm, shown as an inset of Fig. 3a, indicates the increase of aggregation efficiency at higher concentration. The emission spectra exhibit a parallel result. Fig. 3b clearly shows that the emission from aggregates, inferred from the relative intensity at 590 nm, systematically increases with concentration. At concentration of 0.05 mg/mL, the emission from aggregates dominates the emission of agglomerates and isolated chains, which mainly contribute to the intensity at 558 nm (see below). Inset of Fig. 3b shows the increase of emission intensity ratio at 590/558 nm with concentration. The decrease of free volume in the higher concentration is attributed to the increase of aggregate fraction. The higher number of conjugated chain also provides higher probability for chain to stack efficiently, which eventually leads to the aggregation. The following section investigates the nature of each absorption band and emission peak in more detail.

3.2. Separate emissions from various chromophores of MEH-PPV

In this section, photophysics of MEH-PPV in different states, isolated, agglomerated and aggregated chains, are explored. Although chromophores with various conjugation lengths do exist in isolated chain, the emission occurs mostly from the one that possesses lowest HOMO–LUMO energy gap [46,49,50]. Fig. 4a illustrates the emission spectra of extended MEH-PPV chain [39,40] in pure chloroform, recorded by using different excitation wavelengths. According to its absorption pattern in Fig. 1a, using 400 nm photons excites the chromophores with relatively short conjugation length. The resultant emission spectrum consists of a peak at 558 nm with broad vibronic shoulder near 590 nm. Beside a variation of absolute intensity, the pattern is independent of excitation energy. The excitation of long chromophores with 550 nm photons results in the same shape of emission spectrum. However, using the higher excitation energy (400 nm) allows small fraction of short chromophores to emit photons, indicated by a broad emission shoulder with wavelengths ranging from about 400 to 500 nm. Excitation spectra recorded at various emission wavelengths exhibit a shape similar to the absorption pattern. These results indicate significant intrachain energy transfer from short chromophores to the neighboring longer one before the emission process takes place [46]. Theoretical studies suggest that the energy migration process occurs via a sequence of hopping events of excitons along conjugated backbone [49,50]. The measurements of emission and excitation spectra of the agglomerated chains in mixture of chloroform and 60% v/v hexanol provide results similar to that of the isolated one.

The MEH-PPV chains in a mixture of chloroform and 80% v/v hexanol exhibit rather different emission behavior. The emission pattern illustrated in Fig. 4b varies greatly with the

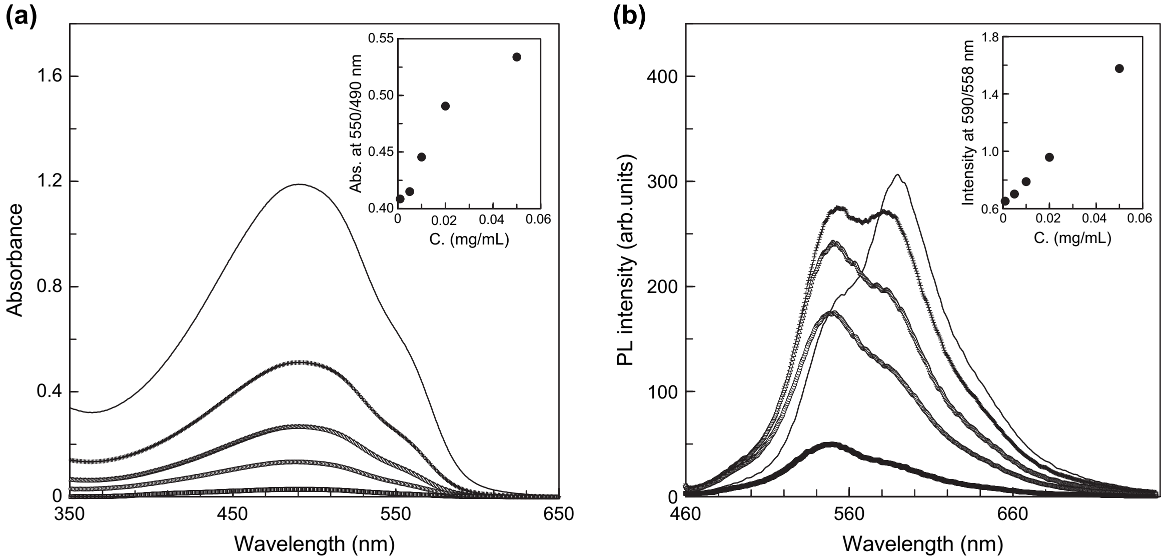

Fig. 3. (a) UV/vis absorption and (b) PL spectra of MEH-PPV in mixture of chloroform and 80% v/v hexanol. Polymer concentrations: (−) 0.05, (+) 0.02, (△) 0.01, (○) 0.005 and (□) 0.001 mg/mL. Insets of (a) and (b) plot ratios of absorbance at 550/490 nm and PL intensity at 590/558 nm, respectively, as a function of polymer concentration. For PL spectra, excitation wavelength of 450 nm was used.

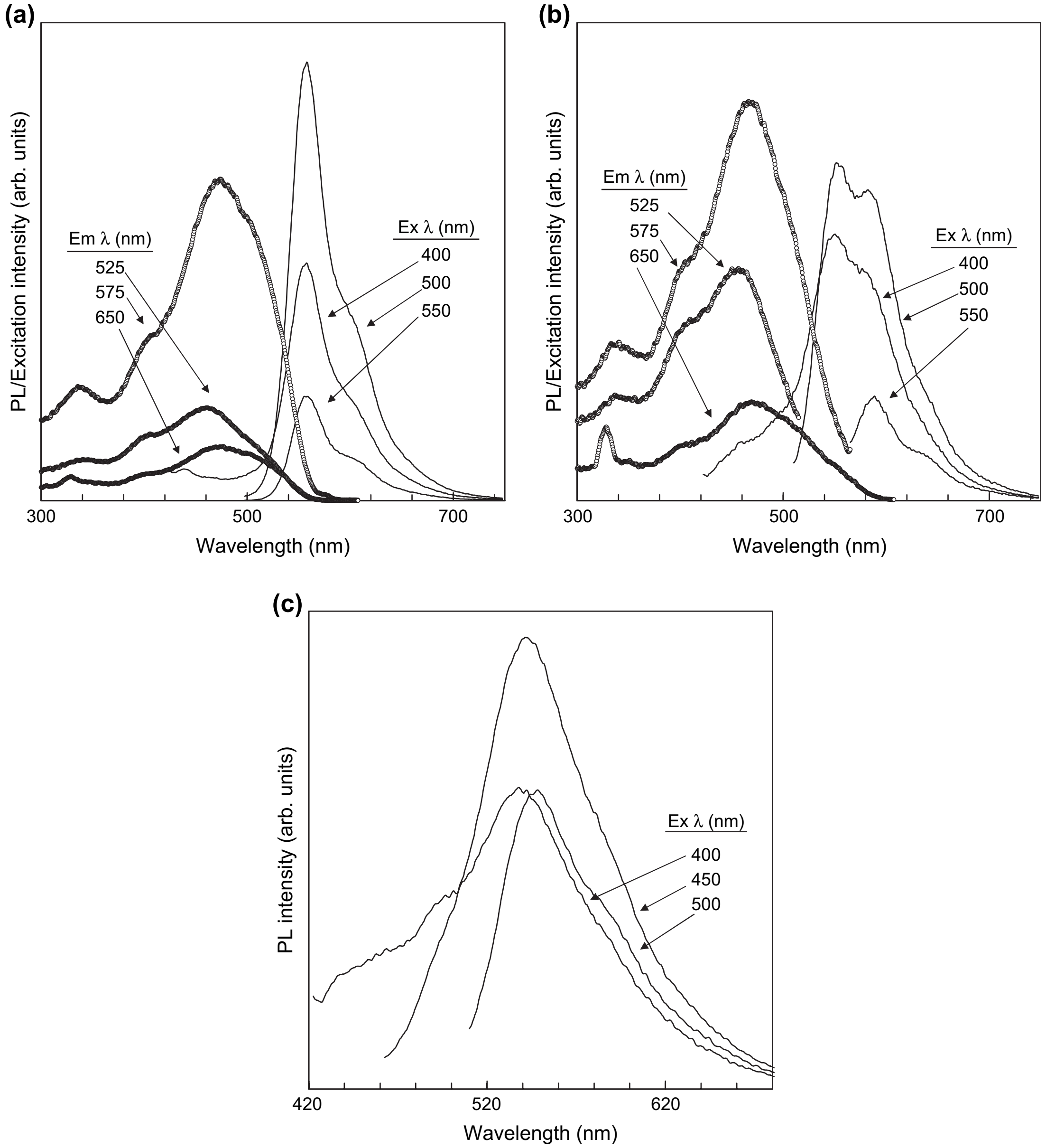

Fig. 4. Excitation (○) and PL spectra (solid line) of 0.01 mg/mL MEH-PPV in (a) pure chloroform and (b) mixture of chloroform and 80% v/v hexanol. The emission spectra were measured using excitation wavelengths (Ex λ) of 400, 500 and 550 nm. The excitation spectra were recorded at fixed emission wavelength (Em λ) of 525, 575 and 650 nm. (c) Emission spectra of filtered solution shown in part (b). For (b,c), the scattering peaks near the edges of spectra are removed for clarity.

excitation energy. Using 400 nm photons for excitation yields the emission pattern with two major peaks at ~558 and 590 nm, similar to that of the isolated chain in pure chloroform. However, the ratio of intensity at 590/558 nm is much higher. The emission from short chromophores also becomes more pronounced, inferred from an increase of the intensity ranging from 400 to 500 nm. Moving excitation wavelength to 500 nm is accompanied by an increase of intensity ratio at 590/558 nm. Further increasing excitation wavelength to 550 nm provides emission pattern with a peak at ~590 nm and broad shoulder near 625 nm. The absorption pattern in Fig. 1a suggests that using the 550 nm wavelength mainly excites the chromophores of aggregates. Therefore, the resultant emission spectrum reflects its electronic structure, which is similar to that of the isolated chain but red shifts by about 30 nm. The overlap of emissions from different electronic species, agglomerates, isolated chains and low energy aggregates, is responsible for the increase of emission intensity ratio at 590/558 nm in this system.

To confirm the origin of each emission peak, excitation spectra are recorded at various emission wavelengths (see Fig. 4b). It is clear that there are multiple absorption processes. The excitation spectrum measured at fixed 525 nm emission wavelength exhibits a peak at 460 nm. It drops to zero at ~550 nm, similar to the excitation spectrum of isolated chain shown in Fig. 4a. The measurement at fixed

650 nm emission wavelength yields a peak at 475 nm. The excitation spectrum also extends to cover large area at low energy region up to 600 nm, which is similar to the red-shift shoulder in its absorption spectrum. These results indicate that the chromophores of aggregates significantly contribute to the emission at low energy region. The chromophores of agglomerates and isolated chains, on the other hand, are mainly responsible for the emission at relatively high-energy region.

Further investigation of electronic properties of isolated chains in the system provides insight into the emission behavior at relatively high-energy region. The filtered solution, containing isolated chains in an unfavorable environment (i.e. a mixture of chloroform and 80% v/v hexanol), exhibits a broad absorption spectrum with peak at ~475 nm (see Fig. 1a). The peak of emission spectra, which varies with excitation energy, ranges from 540 to 550 nm as illustrated in Fig. 4c. The blue shift of absorption and emission spectra relative to that of the MEH-PPV solution in chloroform is attributed to the collapse of isolated chain. Upon addition of hexanol into the polymer solution in chloroform, the chains can take different pathways of molecular rearrangement to minimize unfavorable interactions with the added poor solvent. This includes interchain association (agglomeration and aggregation) and collapse of isolated chain. It has been demonstrated that an isolated chain in collapsed conformation exhibits a decrease of conjugation length relative to that of the extended counterpart [11,17,36,45]. This is mainly due to an increase of physical defects along conjugated backbone, which limits the extent of π-electron delocalization. Studies by Schwartz's group have shown that the decreasing hydrodynamic radius of MEH-PPV in solutions by a factor of 2 causes a blue shift of absorption and emission spectra by ~10 nm [36]. In another system of PPV ionomers, a blue shift of ~50 nm corresponds to ~3 times decrease of its hydrodynamic radius [45].

Our recent study presents thorough investigation of photophysical change in the collapsed coils of MEH-PPV [17]. Series of our experiments suggest that the blue shift is not due to the presence of smaller molecular weight MEH-PPV in the filtered solutions. In addition, the emission spectra of MEH-phenylenevinylene trimers in methanol [47] and other derivatives of phenylenevinylene (PV) oligomers [51,52] exhibit rather different patterns. The emission spectra of PV-oligomers consist of a main 0–0 transition peak with clear 0–1 vibronic shoulder compared to the broad pattern in Fig. 4c. The studies of PV-oligomers also demonstrate that increasing the dielectric constant of solvent results in the decrease of HOMO–LUMO energy gap [51]. The rigid-rod nature of PV-oligomers rules out the possibility of conformational change. Therefore, the blue shift of absorption and emission spectra of our filtered solution is likely to be due to the change of local conformation rather than the increase of solvent polarity. The conjugation length of PV-oligomers increases systematically with number of repeat units [51,52]. Using published empirical correlation between oligomers length and wavelength at maximum absorption, the averaged length of chromophores of isolated MEH-PPV chain in the filtered solution is comparable to that of 2,5-diheptyloxy PV-octamers (8 repeat units) in cyclohexane [51]. Although side chains of the two structures are different, this estimation is still appropriate. The slight change of structure of alkoxy side chain was shown to have minimal effect on electronic structure of conjugated backbone [30]. We note that the averaged length of MEH-PPV chains used in this study is in the order of hundreds of repeat units. The earlier discussion indicates that ~20% of polymers remain in the filtered solution. It is unlikely that relatively large amount of oligomers with 8 repeat units exists in our filtered solution.

In addition to the decrease of conjugation length, the collapse of isolated chain in poor solvent also promotes the emission from chromophores with relatively short conjugation length. Fig. 4c shows that the emission spectrum derived from 400 nm excitation energy constitutes of large fraction of high-energy shoulder (i.e. 400–500 nm). The intensity at this region relative to the main peak is much higher compared to that of the extended chain in chloroform shown in Fig. 4a. The enhanced emission from the short chromophores reflects significant suppression of intrachain energy transfer. The decrease of conformational order of MEH-PPV segments in collapsed coils is probably a major factor responsible for this observation. Our results are consistent with the studies of MEH-PPV containing tetrahedral defects which detect separate emissions from various chromophores upon increasing the magnitude of segment disorder [42,46]. The dependence of emission pattern on excitation energy supports the existence of multiple emitters which absorb light at different energy regions. An investigation of this issue in details was presented in our previous report [17].

The photophysics of various electronic species of MEH-PPV are further explored by using pure alcohol as a solvent. Using a homologous series of linear alcohols allow systematic variation of polarity and molecular architecture. The absorption spectra of MEH-PPV in butanol, hexanol and octanol illustrated in Fig. 5 exhibit a pattern, consisting of a broad peak at ~490 nm and shoulder at ~550 nm. Filtration of the solutions by nylon membrane (0.45 μm pore size) causes the 550 nm shoulder to disappear while the main absorption band at 490 nm significantly drops. Absorption spectra of the filtered solutions exhibit a blue shift as well. These results, consistent with that of the solvent–nonsolvent system discussed earlier, support the existence of aggregates, agglomerates and collapsed coils in poor solvents. Magnitude of the blue shift detected in the filtered solutions increases with decreasing solvent quality. This corresponds to the systematic increase of extent of chain collapse in poor solvents ranging from octanol, hexanol and butanol [17]. The ratio of absorbance at 550/490 nm, reflecting aggregates/non-aggregates ratio, also varies with quality of solvents. The discussion on this issue is postponed to the following section.

Since the MEH-PPV used in this study exhibits rather broad molecular weight distribution, one may expect the relatively short polymeric chains to preferably dissolve in these poor solvents. These short chains could be responsible for the blue shift of absorption spectra detected in the filtered solutions. To demonstrate that this was not the case, a series of

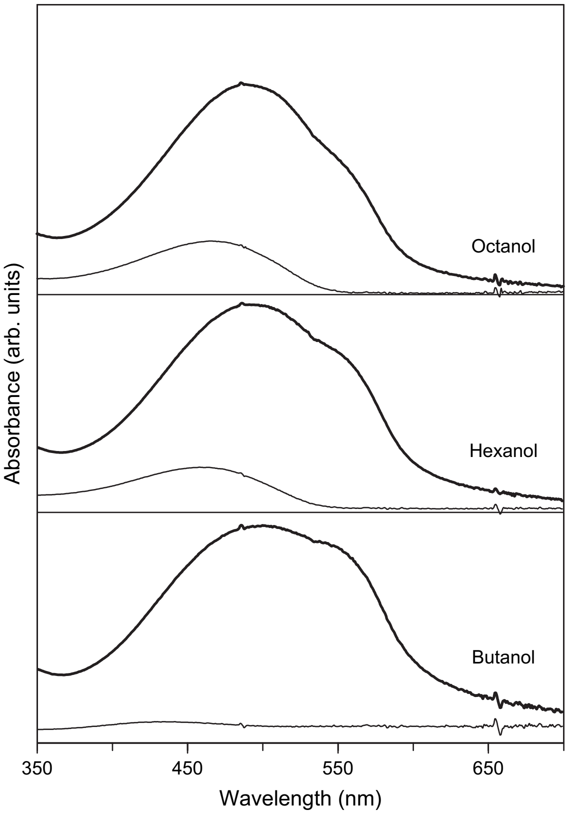

Fig. 5. UV/vis absorption spectra of 0.01 mg/mL MEH-PPV in pure alcohols before (thick lines) and after (thin lines) filtration by using nylon filter with 0.45 μm pore size. Solvents are shown on the right hand side of each spectrum. Spectra are shifted vertically for presentation.

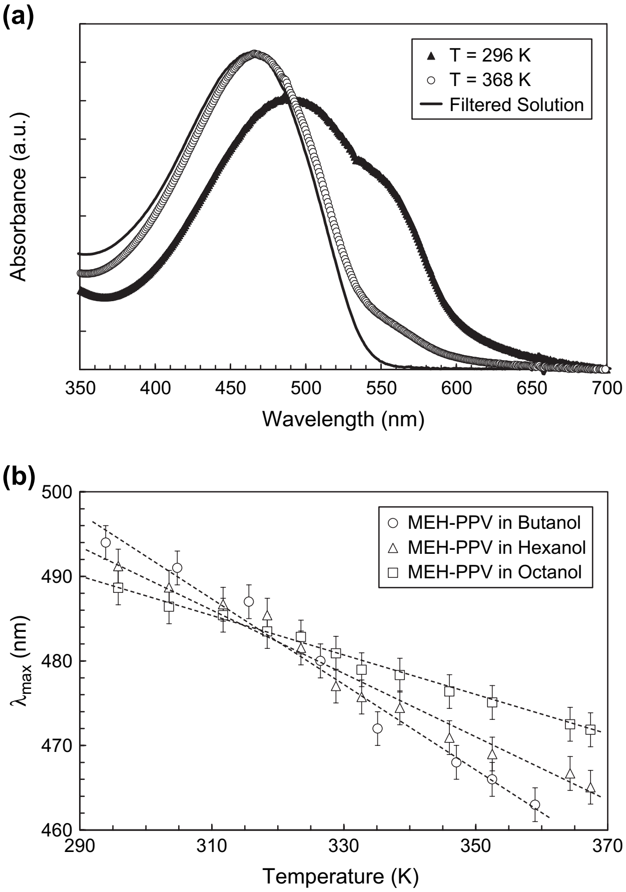

Fig. 6. (a) Absorption spectra of 0.01 mg/mL MEH-PPV in hexanol measured as a function of temperature. The normalized absorption spectrum of the filtered solution is included for comparison. (b) Plots of λ_{max} of MEH-PPV absorption spectra in different alcohol solvents as a function of temperature. At high temperature the λ_{max} reaches the value of the respective filtered solutions. Dashed lines are for guiding.

experiments were carried out. The MEH-PPV aggregates in unfiltered solutions dissociate upon increasing temperature, indicated by the decrease of absorbance at 550 nm as shown in Fig. 6a. At 95 °C, only small fraction of aggregates exists in the solution. Most of the polymeric chains are isolated at this elevated temperature. It is clear that its absorption spectrum matches that of the filtered solution. We observe the same results from the studies of MEH-PPV solutions in octanol and butanol. Fig. 6b shows a gradual blue shift of absorption maxima of these solutions upon increasing temperature. At high temperature, the value reaches the λ_{max} of absorption spectra of respective filtered solutions. These results indicate that isolated MEH-PPV chains in the filtered and unfiltered solutions exhibit the same electronic properties. Our previous study systematically investigates the photophysics of isolated chains in these alcohol solvents, indicating that the blue shift of absorption and emission spectra is due to the collapsed chains [17].

The measurements of excitation and emission spectra of MEH-PPV in hexanol (see Fig. 7a) indicate the existence of various chromophores consistent with the results observed in the solvent–nonsolvent system. The emission spectrum of aggregates recorded by using excitation wavelength at 550 nm still exhibits a peak and shoulder at ~590 and 625 nm, respectively. However, the intensity at high-energy region (400–500 nm), mainly contributed from short chromophores, is much more pronounced. The emission spectrum derived from 400 nm excitation wavelength shows a peak at ~530 nm with two shoulders at ~500 and ~465 nm. The emission spectrum of filtered solution measured by using the 400 nm excitation wavelength exhibits similar pattern as illustrated in Fig. 7b. This indicates that the two shoulders at relatively high-energy region belong to the isolated chain in collapsed conformation. The absorption peak of filtered solution is at ~465 nm (see Fig. 5) while the peak of emission ranges from 530 to 540 nm, depending on the excitation energy. The magnitude of blue shift of these spectra is higher than that of the solution in mixture of chloroform and 80% v/v hexanol, indicating larger extent of chain collapse. Therefore, the intrachain energy transfer is further suppressed in this more segmental disorder conformation, allowing larger fraction of short chromophores to emit photons [17,42,46]. The detection of the high-energy shoulders is unlikely due to hydrogen bonding between the alkoxy side chain and hydroxy group of the alcohol. The emission spectra of isolated MEH-PPV chain in cyclohexane and hexane, in which the hydrogen bonding is not possible, still exhibit similar structure [17].

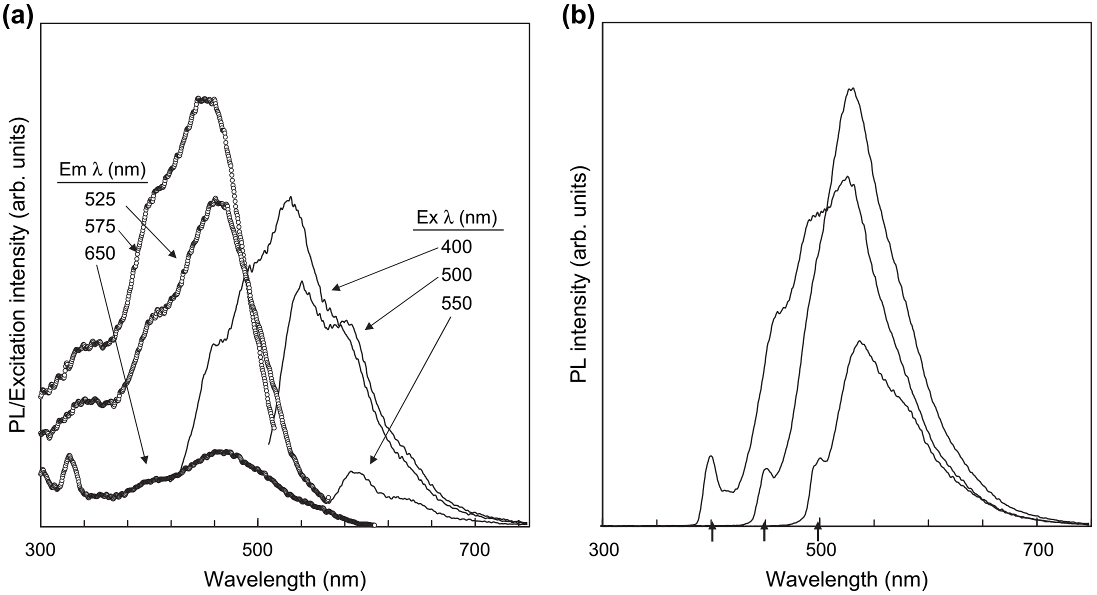

Fig. 7. (a) Excitation (○) and PL spectra (solid line) of 0.01 mg/mL MEH-PPV in pure hexanol. Spectra were recorded at different emission wavelengths (Em λ) and excitation wavelengths (Ex λ) as shown in the plot. Scattering peak near the edge of spectra is removed for clarity. (b) PL spectra of the filtered solution of part (a) recorded by using different excitation wavelengths are indicated by arrows (400, 450, 500 nm).

From the previous discussions, we can summarize the mechanism of MEH-PPV chain organization upon decreasing solvent quality in Fig. 8. The decrease of polymer solubility in poor solvents drives the isolated chains to associate into large particles. The process is expected to take place in a random fashion. Therefore, large fraction of the chains assembles into networks with slight change of conformation. Segments of the conjugated backbones that stack efficiently result in a red shift of the spectra while the one that connect loosely leaves electronic properties unaltered. Theoretical studies have shown that the phenylenevinylene segments in aggregates arrange in cofacial geometry with a shift of one segment along chain axis [11,12,39]. Degree of the shift is an important factor for the formation of J-type aggregates, which cause red-shift peak in absorption and emission spectra. This issue was investigated in detail by Siddiqui and Spano [12]. The

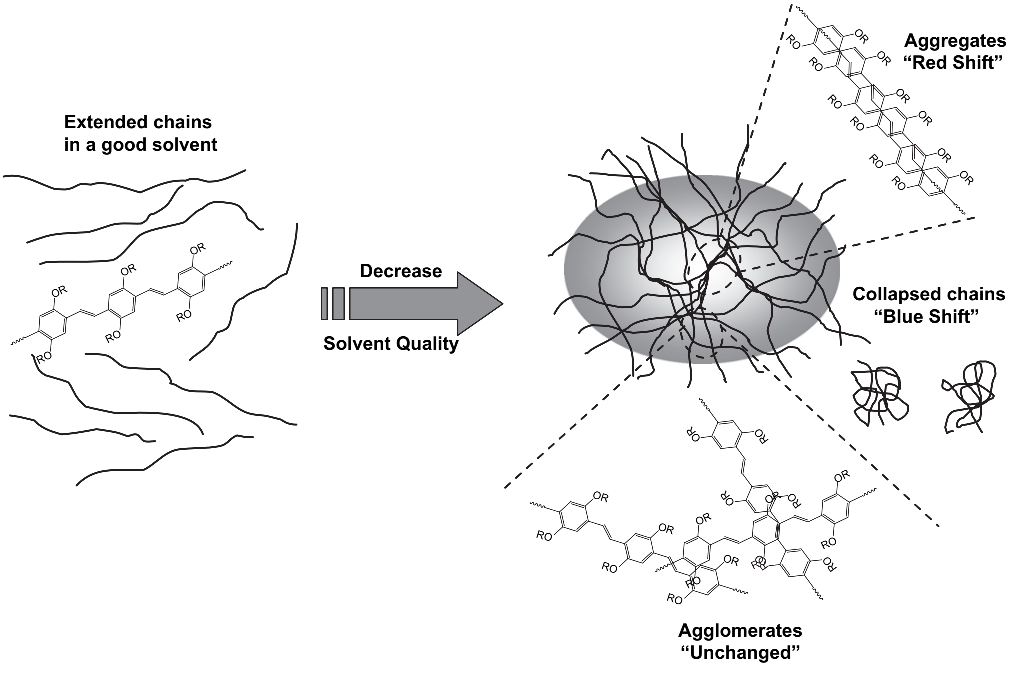

Fig. 8. Schematic representation of the association and the collapse of isolated chains in poor solvents. The large polymeric particle constitutes of aggregated and agglomerated sites. The aggregate causes a red shift of the absorption and PL spectra while the agglomerate leaves electronic properties of chromophores unchanged. The collapse of isolated chains results in a blue shift of spectra.

aggregated and agglomerated sites distribute randomly in the large polymeric particles. Small fraction of isolated chains collapses in poor solvent, which results in a blue shift of absorption and emission spectra. The extent of chain collapse dictates magnitude of conjugation and energy transfer along conjugated backbone.

3.3. Role of chain conformation on interchain association and energy transfer

Our previous study has shown that conformation of MEH-PPV chain in alcohols can be systematic controlled by varying the polarity of solvent [17]. In this section, role of individual chain conformation on the behavior of interchain association is explored. Fig. 9a illustrates absorption spectra of MEH-PPV in a homologous series of linear alcohols ranging from methanol to dodecanol. All spectra constitute of two broad bands with peak at ~490 and 550 nm. By fitting the spectra to Gaussian functions as shown in Fig. 10a, the two absorption bands can be separated. The discussions in earlier section suggest that the absorbance at 490 and 550 nm is proportional to the concentration of non-aggregated and aggregated chains, respectively. To explore relationship between their concentrations and solvent polarity, relative areas of the two bands are plotted as a function of dielectric constant of the alcohols (see inset of Fig. 10a). The plot of absorbance ratio at 550/490 nm illustrated in Fig. 10b shows the same trend. An overlap of the peaks only causes absorbance ratio to be higher than the ratio of integrated areas. Error bars shown in the plot are estimated from several measurements of solutions prepared independently. Serial dilution of polymer concentration from 0.50 to 0.006 mg/mL slightly affects the absorbance ratio but its value is still within the error bar.

Fig. 10b clearly shows that concentration ratio of the two electronic species, inferred from the ratio of absorbance at 550/490 nm, varies with polarity of the alcohol solvents. For long-chain alcohols (i.e. dodecanol to butanol) with relatively low dielectric constant, the plot exhibits a linear relationship with positive slope. This indicates a linear increase of aggregate concentration relative to that of non-aggregates upon increasing solvent polarity. A systematic decrease of MEH-PPV solubility, a major driving force for the interchain association, is attributed to this behavior. Filtration of the solutions (see Fig. 5) detects a gradual decrease of isolated chain concentration in the more polar solvent, confirming the decrease of solubility.

Although further increasing the solvent polarity continues to cause the polymer solubility to diminish, the relative concentration of aggregates appears to be hardly affected. The absorption spectra of MEH-PPV in methanol, ethanol, propanol and butanol in Fig. 9a exhibit almost the same shape. Filtration of these solutions detects only trace amount of isolated chains. A plateau of the plot in Fig. 10b indicates the independence of aggregate/non-aggregate ratio on the dielectric constant of solvent. In this region, unfavorable polymer–solvent interactions force most of the chain to assemble into large particles. The chain organization to form aggregated sites (see Fig. 8), however, is controlled by other parameters in addition to the decrease of polymer solubility. Since the aggregation requires specific stacking of multiple conjugated segments

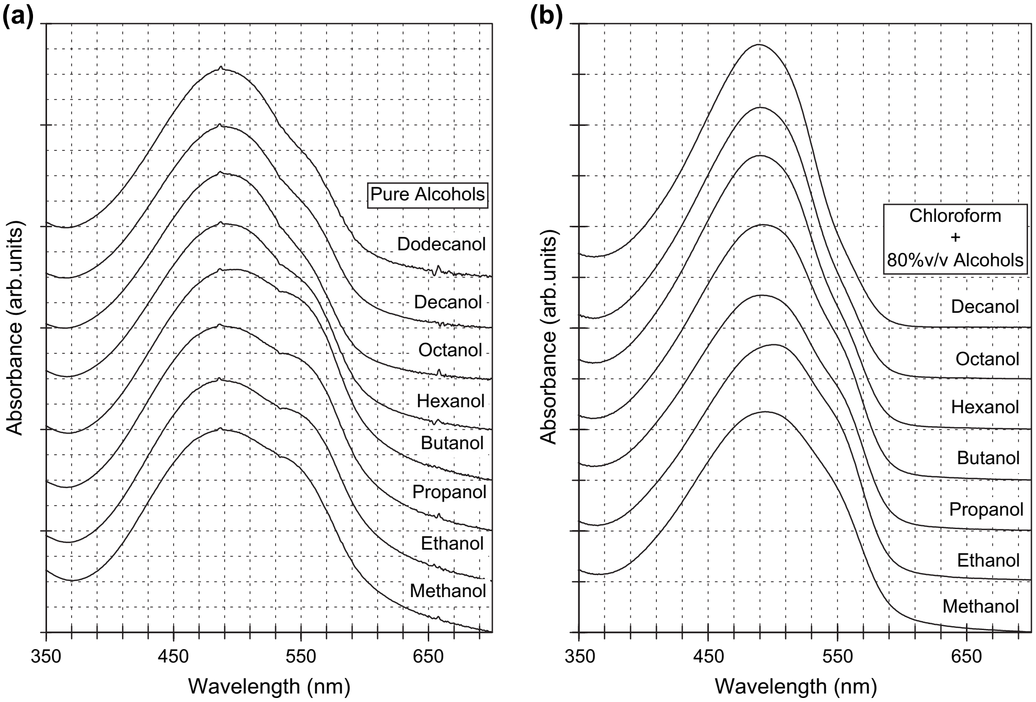

Fig. 9. Absorption spectra of MEH-PPV in (a) a homologous series of alcohols and (b) mixtures of chloroform and 80% v/v alcohols. Polymer concentration is fixed at 0.01 mg/mL in all solutions. Alcohol solvents are shown on the right hand side of each spectrum. Spectra are normalized and shifted vertically for presentation.

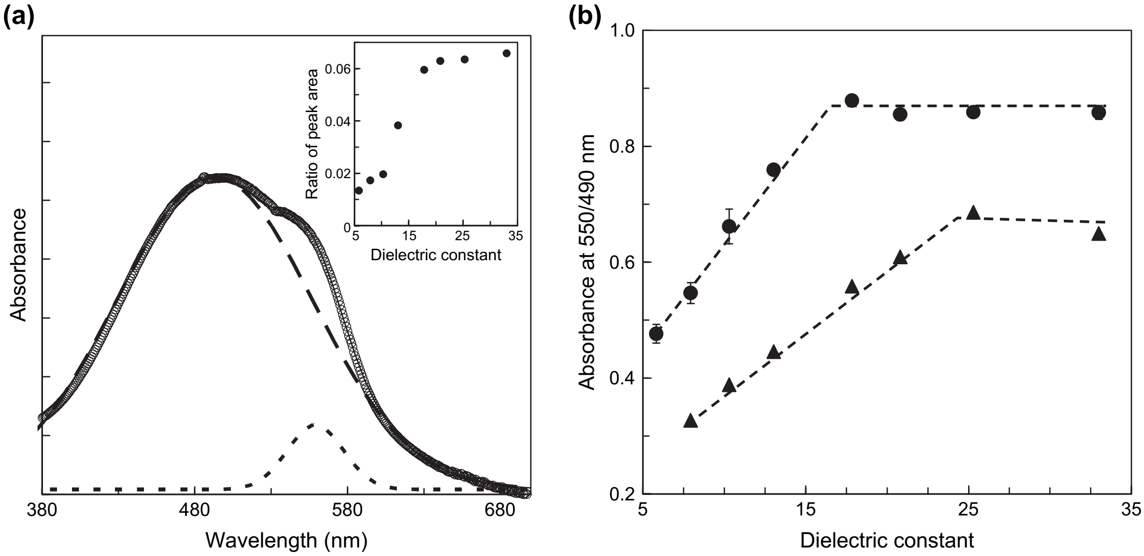

Fig. 10. (a) The deconvolution of absorption spectrum by using Gaussian functions. Inset shows ratios of integrated peak area (550/490 nm) as a function of dielectric constant of the alcohols. (b) Plot of absorbance at 550 nm relative to 490 nm as a function of dielectric constant of alcohols. Solvents: (●) pure alcohols and (▲) mixtures of chloroform and 80% v/v alcohols. Dashed lines are for guiding.

[11,12], the conformation of individual chains has to play an important role. Isolated chain of MEH-PPV can adopt extended or collapsed conformations in solution, depending on local polymer–solvent interactions [39,40]. Study by using methods of dynamic light scattering and fluorescence spectroscopy suggests that the aggregation is more efficient when the MEH-PPV chains are in more open conformation [10,36]. Our previous study on isolated chain indicates that the magnitude of chain collapse reaches extreme in methanol, ethanol, propanol and butanol [17]. Therefore, the significant collapse of individual chain in these solvents is probably a major factor that inhibits efficient stacking of the conjugated segments.

To further confirm our results, we investigated the aggregation behavior of MEH-PPV in mixtures of good and poor solvents. The solvent–nonsolvent system allows all solutions to be prepared from the same stock solution. Fig. 9b illustrates absorption spectra of MEH-PPV in mixtures of chloroform and 80% v/v alcohols. The polymer concentration is kept constant while structure of alcohol is changed from decanol to methanol. The variation of absorbance ratio at 550/490 nm with dielectric constant of the alcohols is shown in Fig. 10b. Similar to the results obtained from the polymer solutions in pure alcohols, the plot constitutes of two regions, linear and plateau. However, slope of the linear line is smaller and the plateau is reached in the mixtures using ethanol and methanol. Values of the absorbance ratio are also smaller. These discrepancies are attributed to the presence of chloroform, which is a better solvent than the alcohols. The better solvation of chloroform probably causes the decrease of aggregate concentration compared to the solutions in pure alcohols. The results in previous section also indicate that the extent of chain collapse is smaller in the solvent–nonsolvent system, allowing the plateau to be reached at higher polarity of alcohols. The observation of plateau region, corresponding to the limited aggregation efficiency, further supports the role of chain conformation on the interchain aggregation.

Powder sample of MEH-PPV consists of various chains with different molecular weights. One can expect the high-polarity alcohols to dissolve mostly the fraction of short chain molecules, which could be responsible for the observed results. However, the average molecular weight of our MEH-PPV is relatively small, allowing the powder sample to be dispersed thoroughly in the studied alcohols. The solutions were then subjected to serial dilution without filtration, preserving all molecular weights. In addition, the experiments on solvent–nonsolvent system were carried out using the same stock solution. Therefore, the effect of molecular weight variation on our results is expected to be minimal. In fact, the molecular weight effect on aggregation behavior was previously investigated by Rothberg's group [19]. Parallel studies of PPV derivative (20–30 repeat units) and its corresponding pentamer showed quantitatively similar results on the relative aggregate concentration.

The measurements of emission spectra provide results consistent with that of the absorption spectra. Insight information on energy transfer and conformation of individual chain in associated polymeric particles is also obtained. Fig. 11 illustrates the emission spectra of MEH-PPV in mixtures of chloroform and 80% v/v alcohols recorded by using excitation wavelengths at 400 and 500 nm. Although using the 400 nm photons mostly excites short chromophores of MEH-PPV, the emissions from other chromophores with longer conjugation length are still detected. The emission spectra of all solutions constitute of two major peaks at ~550 and ~590 nm with broad shoulder at relatively high-energy region (400–500 nm). Our previous discussions demonstrate that the emission intensity at wavelength shorter than 550 nm arises mostly

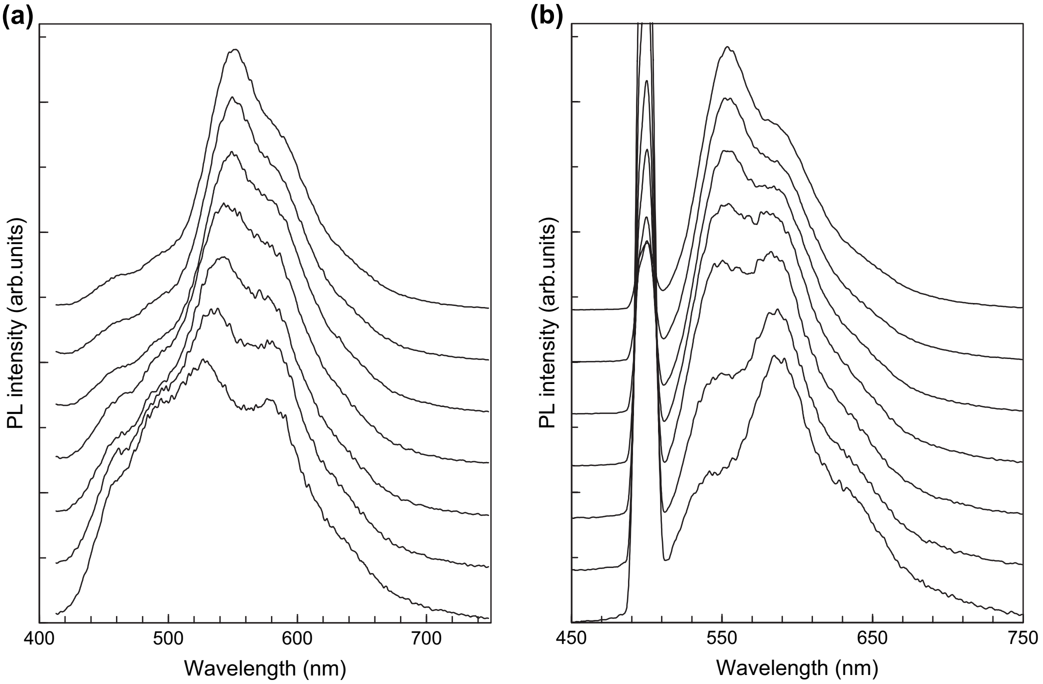

Fig. 11. Emission spectra of MEH-PPV in mixtures of chloroform and 80% v/v alcohols (alcohol solvents from top to bottom: decanol, octanol, hexanol, butanol, propanol, ethanol, and methanol). Polymer concentration is fixed at 0.01 mg/mL in all solutions. All spectra are normalized and shifted vertically for clarity. Excitation wavelengths are (a) 400 and (b) 500 nm. Sharp peak at 500 nm in (b) is due to the scattering of excitation light.

from the chromophores of non-aggregated chains while the emission from aggregates contributes to the intensity above 550 nm.

Fig. 11a clearly shows that increasing the polarity of the solvent is accompanied by the increase of intensity ratio at 590/550 nm. The increase of intensity ratio at 590/550 nm is consistent with the measurements of absorption spectra, which detect systematic increase of aggregate concentration upon increasing solvent polarity. The measurements of emission spectra by using excitation wavelength at 500 nm shown in Fig. 11b further confirm the results. At this excited energy the emission from short chromophores of non-aggregated chains is significantly suppressed, allowing the emission from aggregates to dominate. Systematic increase of relative intensity at 590 nm is clearly observed. The measurements of emission spectra also detect systematic decrease of the emission intensity upon increasing solvent polarity. The decrease of fluorescence efficiency is consistent with the increase of interchain association [20].

In addition to the increase of intensity at 590 nm upon increasing solvent polarity, the emission spectra in Fig. 11a also show simultaneous increase of the intensity ranging between 400 and 500 nm. The emission spectrum of MEH-PPV in mixture of chloroform and 80% v/v methanol clearly exhibits two shoulders at ~460 and ~490 nm. The detection of these high-energy shoulders implies that the energy transfer from the excited electronic species to neighboring chromophores with longer conjugation length is significantly suppressed. This result can be explained by considering the conformation of individual chain within the associated polymeric particle. The decrease of solvent quality can cause conjugated chain to collapse. This implies the increase of segmental disorder, an important parameter that diminishes efficiency of intrachain energy transfer [42,46]. One can also expect the interchain association in poor solvents to promote the interchain energy transfer, which is a more efficient pathway compared to the intrachain process [49,50]. This is the case for conjugated polymer in thin film where the conformation of individual chains is probably not significantly affected. In addition, mechanism of the interchain energy transfer requires the conjugated backbones to arrange in a cofacial fashion [50]. In our system, the associated polymeric particles constitute of only small fraction of aggregated sites. Therefore, the suppression of intrachain energy transfer is a dominant factor.

The suppression of intrachain energy transfer is more pronounced when the conformation of individual chain is forced to collapse to larger extent. Fig. 12a illustrates emission spectra of MEH-PPV in a homologous series of pure alcohols measured by using excitation wavelength of 400 nm. In all solution, the emission from short chromophores (400–500 nm) is higher compared to the results observed in the solvent–nonsolvent systems. The emission spectra of solutions in methanol, ethanol and propanol clearly exhibit large peak at ~500 nm. The measurements of emission spectra using excitation wavelength of 500 nm still detect systematic increase of aggregate concentration upon increasing solvent polarity as shown in Fig. 12b. The intensity ratio at 590/550 nm reaches plateau in high-polarity alcohols consistent with the results of absorption spectra.

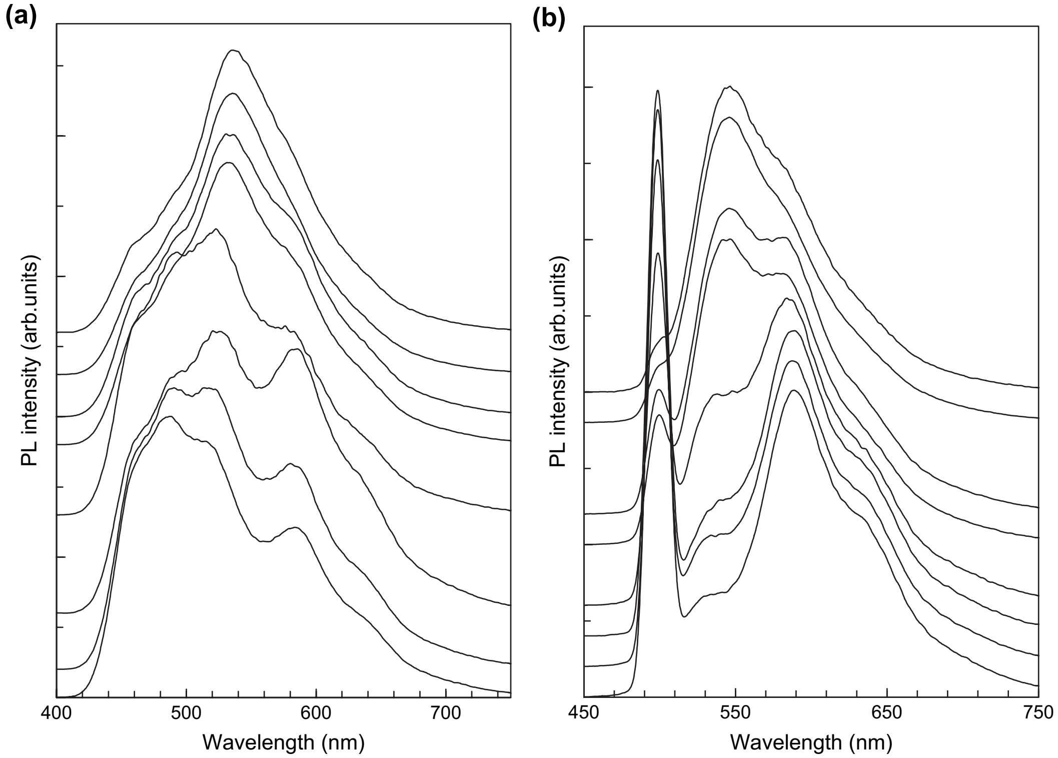

Fig. 12. Emission spectra of MEH-PPV in a homologous series of alcohols (solvents from top to bottom: dodecanol, decanol, octanol, hexanol, butanol, propanol, ethanol, and methanol). Polymer concentration is fixed at 0.01 mg/mL in all solutions. All spectra are normalized and shifted vertically for clarity. Excitation wavelengths are (a) 400 nm and (b) 500 nm. Sharp peak at 500 nm in (b) is due to the scattering of excitation light.

4. Conclusions

We have shown that the aggregation of MEH-PPV in poor solvents results in a red-shift peak in absorption and emission spectra while the agglomeration does not affect electronic properties. The aggregated and agglomerated sites are believed to distribute randomly in large polymeric particles. The collapse of isolated chains in poor solvents is indicated by a blue shift of the absorption and emission spectra. The emission spectra of MEH-PPV in poor solvents are demonstrated to constitute of overlapped emission patterns that belong to various chromophores with different conjugation lengths. The organization of isolated chains into aggregates strongly depends on the extent of chain collapse. In relatively long-chain alcohols, the ratio of aggregate concentration relative to that of the non-aggregates linearly increases with decreasing solvent quality. The increase of relative aggregate concentration reaches plateau in the high-polarity alcohols, attributed to the extreme collapse of polymeric chains. The collapse of individual chain in associated polymeric particle is also found to cause the decrease of energy transfer between electronic species in the system. This allows the emission of high-energy chromophores to take place.

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