

Spectroscopic Study of Photophysical Change in Collapsed Coils of Conjugated Polymers: Effects of Solvent and Temperature

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ABSTRACT: A relationship between conformation and photophysics of poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylenevinylene] (MEH–PPV) in dilute solution was investigated by utilizing UV/vis absorption, excitation, and emission spectroscopy. By tuning polymer–solvent interactions, a control of conjugation length which relates to state of chain collapse is achieved. Position of absorption and emission spectra can be systematically moved within 60 nm by using a series of alcohols and aromatic solvents as well as mixed solvents. In addition to a decrease of conjugation length, the collapsed chain exhibit optical characteristics different from that of the extended counterpart. While a single type of emitter is present in the extended chain, separate emission from multiple emitters with various conjugation lengths is detected from the collapsed coils. Fluorescence decay measurements support the presence of multiple emitters. Studies of UV/vis absorption and photoluminescence upon increasing temperature detect a blue shift of transition energies and a decrease of absorption and emission efficiency. In addition, rate of the shift is found to decrease with increasing magnitude of chain collapse.

Introduction

The unique properties of conjugated polymers including high photo- and electroluminescence and semiconducting^{1–4} render them candidates for various applications such as organic light-emitting diodes (OLED),^{1,4} molecular wires² in molecular scale electronics, and chemical sensors.^{3,5,6} To realize its full potential, researchers have investigated molecular parameters that dictate photophysical behaviors of conjugated polymers. In this study we explore relationship between local structure of conjugated polymers, controlled by tuning local polymer–solvent interactions and their photophysical processes. The well-known poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylenevinylene] (MEH–PPV) has been investigated. Its chemical structure shown in Figure 1 is constituted of aromatic backbone with slightly polar alkoxy side chains, enabling us to select a wide range of molecules to vary magnitude of the polymer–solvent interactions. Our finding offers one way of controlling effective conjugation length without having to modify chemical structure. The MEH–PPV chain in the collapsed state also shows excitation and emission patterns differing from previous reports. We propose origins of these characteristics based on its evolution with the expansion of polymer coil, accompanied by results of fluorescence decay dynamics.

Studies have shown that photophysics of conjugated polymers dissolved in solvents can alter substantially due to conformational change of isolated chains^{7–20} and interchain aggregation.^{21–30} In the aggregated state, the close proximity allows π -electrons to delocalize over multiple stacked segments of different chains in both electronic ground and excited states.⁷ The extent of π -electron delocalization is significant enough to form novel electronic species exhibiting lower HOMO–LUMO energy gap relative to that of an isolated chain. Therefore, the signature of the aggregation is the detection of distinct red-

shift absorption and emission band.^{16,22–26,29,30} However, the origin of the red-shift band is sometimes suggested to arise from the collapse of isolated chains^{14,27} and planarization of phenyl rings within the chromophore due to the local confinement.²⁹

Conjugated polymers can twist to form various conformations in solution and thin film.^{7–10,16,17,31–33} The twisted points, its number increase with the magnitude of chain collapse, prevent the delocalization of π -electrons over the entire chain. Therefore, isolated chain of conjugated polymer can be described as an ensemble of conjugated segments or chromophores linked by many “physical defects”.^{7,9,10} The extent of π -electron delocalization in each chromophore reflects the effective conjugation length of the polymeric chain. The state of chain collapse can be controlled by utilizing many approaches such as attaching different side chains,¹⁷ tuning local polymer–solvent interaction,^{7–9,16,34,35} and introducing the so-called “tetrahedral defects” in the backbone.^{14,36,37} The collapse of conjugated chain has been reported to cause the decrease of conjugation length.^{7,16,34,35} For example, the decrease of hydrodynamic radius of MEH–PPV by a factor of ~ 2 causes its absorption and emission spectrum to blue-shift by ~ 10 nm.¹⁶

In this contribution we elaborate in more detail on the relationship between conformation and photophysics of MEH–PPV. The magnitude of chain collapse is induced to extreme where a blue-shift of about 60 nm occurs. In the collapsed state, separate emissions of various chromophores within the same chain are detected. We also take a step forward to demonstrate a way to systematically select solvents that can finely tune the location of absorption and emission spectra as much as 60 nm.

Experimental Section

MEH–PPV was synthesized in our laboratory following procedure described in the literature.³⁸ The number-averaged molecular weight (M_n) (GPC with polystyrene standard) is 66 000 g/mol with polydispersity (M_w/M_n) of 4.2. Freshly prepared solutions were used in all measurements. Solutions of MEH–PPV were prepared by adding solvents (AR grade) to powder sample and sonicating for

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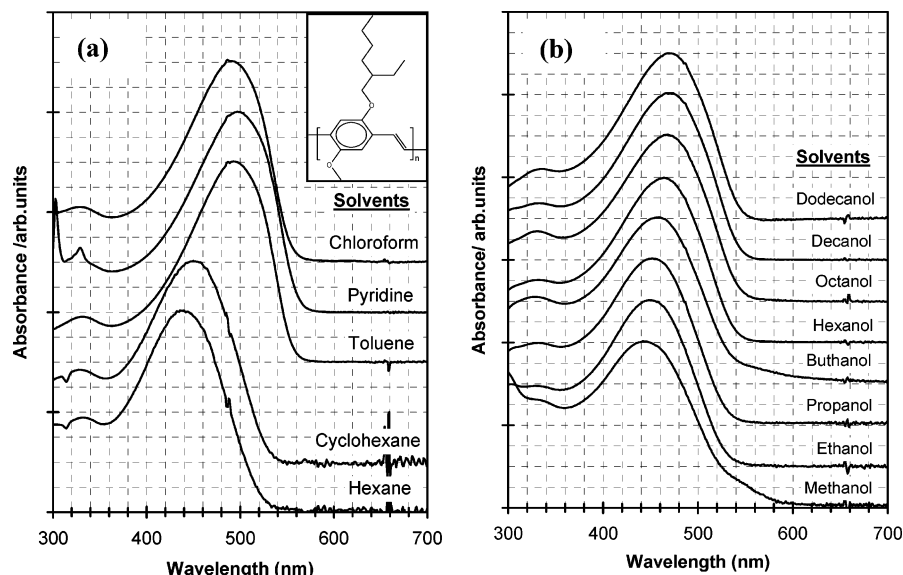


Figure 1. Absorption spectra of MEH-PPV (its structure shown as the inset) in series of solvents shown on the right side of each spectrum. All spectra were normalized to same intensity and shifted vertically for clarity.

an appropriate amount of time. In some cases residual solids in solutions were filtered out by using a $0.45\ \mu\text{m}$ pore size nylon filter. Polymer concentrations ranged from 0.0005 to 0.05 mg/mL. Absorption spectra were recorded on a double-beam Perkin-Elmer Lambda 20 and single-beam Analytica Specord 100 UV/vis spectrometers using a 1 mm thick cuvette. Measurements of photoluminescence emission and excitation spectra were carried out on a Perkin-Elmer LS55. The temperature controller using the water circulation system was connected to a sample holder to allow variable temperature measurements. The temperature, which can be controlled to $\pm 0.5\ ^\circ\text{C}$, was measured directly from solution. Fluorescence decay measurements were performed on Fluorocube (Horiba Jobin Yvon Instrument).

Results and Discussion

Effect of Solvent Quality on Conjugation Length. The state of polymeric chain collapse in solution is dictated by local interactions with solvent. In a poor solvent, system minimizes interfacial contact due to unfavorable polymer-solvent interactions, reflected by a decrease of solubility, forcing chains to adopt a collapsed coil conformation. The absorption spectrum of a dilute solution of MEH-PPV in chloroform where its peak is at about 495 nm is broad and featureless, as shown in Figure 1. Characteristics of spectra resemble results from other studies investigating various MEH-PPVs with more than 10 times difference of molecular weight.^{16,17,20,25–27,39} This is consistent with the description of conjugated polymers that can be viewed as an ensemble of individual chromophores made of a small conjugated segment. Therefore, molecular weight is an insignificant factor on its average effective conjugation length.

The broadness and λ_{max} of the absorption spectra of MEH-PPV in chloroform provide insight about the distribution of chromophores and the concentration of tetrahedral defects within the conjugated backbone. It is well accepted that single molecule of MEH-PPV can be considered as a chain consisting of hundreds of quasi-localized chromophores, which are connected by chemical and structural defects.¹⁰ The conjugation length of each chromophore ranges from 10 to 17 repeat units.⁴² Since the absorption of photons excites various chromophores, the absorption spectra exhibit a broad pattern that envelops many bands of the individual chromophore.³⁷ The synthesis of MEH-PPV can introduce some randomly located tetrahedral defects along the chain, which is an important factor dictating the

magnitude of chain collapse. The analysis of the absorption spectra in chloroform ($\lambda_{\text{max}} \sim 495\ \text{nm}$) according to the published correlation of absorption maxima vs mole percent of tetrahedral defects estimates about 4 mol % of the chemical defects in our MEH-PPV.³⁷

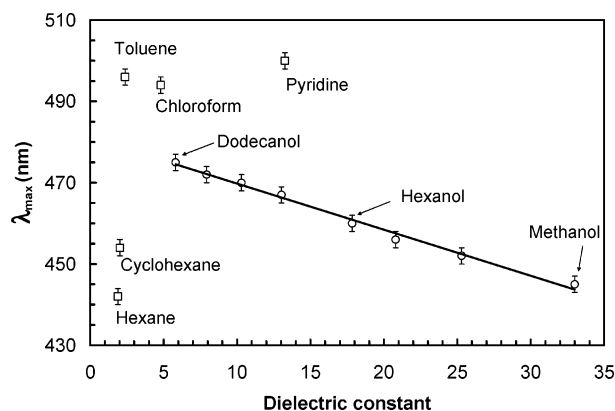
The MEH-PPV molecule is constituted of phenyl rings, which enable it to dissolve in common aromatic solvents. Toluene and pyridine dissolve the polymer to a considerable amount, but still ~ 10 times less than the chloroform. In recent theoretical studies, the MEH-PPV chain appears to coil in the toluene while the chloroform allows the extended conformation.^{8,9} However, the pattern of its absorption spectra in the two aromatic solvents is similar to that of the chloroform solution. The peak slightly shifts to 500 nm. This indicates a small increase of the effective conjugation length despite the coiling of chain. The rationalization for this observation could arise from intrinsic optical properties of the chromophore that derives from a small segment of backbone, only about 10–17 monomer units.^{17,42} In toluene and pyridine, the extent of chain coiling may not be significant enough to alter the average conjugation length. Another potential explanation concerns dynamics of phenyl ring rotation in the backbone. A twist of π -orbitals out of plane interrupts the delocalization of π -electrons.²⁹ Our recent NMR measurements detect slower dynamics of phenyl ring rotation in the toluene and pyridine solutions.⁴⁰ Therefore, a more statistically coplanar arrangement of phenyl rings could be one important factor promoting the conjugation along the backbone.

The state of chain collapse can be induced to extreme by dispersing MEH-PPV in very poor solvents. Cyclohexane and hexane can partially dissolve the polymer, manyfold less than the aromatic solvents. In the tight local chain confinement, change of chromophore properties is observed. The peak of absorption spectra shifts to 441 and 453 nm in hexane and cyclohexane, respectively. The blue shift of ~ 60 and $50\ \text{nm}$ in these poor solvents corresponds to a significant decrease of the effective conjugation length. For comparison purposes, this shift of the spectrum is comparable to about 3 times the decrease of the hydrodynamic radius of PPV ionomers.^{34,35} It is also on the same magnitude of introducing about 25–30 mol % of the tetrahedral defects in the main chain.³⁷ Spectroscopic data of MEH-PPV dissolved in various solvents are presented in Table 1.

Table 1. Spectroscopic Data of MEH-PPV Dissolved in Solvents with Different Dielectric Constants^a

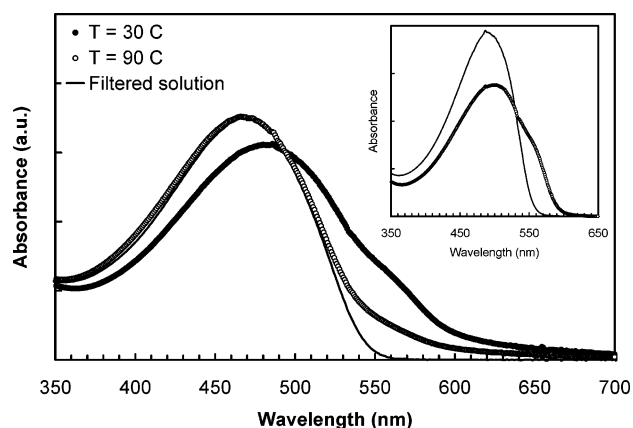
solvents	dielectric constant	$\lambda_{\text{max(abs)}} (nm)$	$\lambda_{\text{max(ems)}} (nm)$ ($\lambda_{\text{ex}} \sim \lambda_{\text{max(abs)}}$)	$\lambda_{\text{max(ems)}} (nm)$ ($\lambda_{\text{ex}} > 500 nm$)
chloroform	4.8	494	558 (607)	558 (607)
toluene	2.4	496	558 (603)	558 (603)
pyridine	13.3	500	563 (609)	563 (609)
cyclohexane	2.0	454	520 (493, 458)	527
hexane	1.9	442	517 (493, 458)	524
methanol	33.0	445	519 (496, 460)	526
ethanol	25.3	452	521 (496, 460)	529
propanol	20.8	456	523 (496, 460)	530
butanol	17.8	460	524 (496, 460)	531
hexanol	13.0	467	541	543
octanol	10.3	470	545	547
decanol	7.9	472	548	549
dodecanol	5.8	475	549	550

^a Emission spectra were recorded using different excitation wavelength (λ_{ex}). Numbers in parentheses represent the location of shoulders in emission spectra.

**Figure 2.** Plot of peak position (λ_{max}) of the absorption spectra in Figure 1 as a function of dielectric constant of solvents. Data obtained from solutions of alcohols are fitted to the linear equation $y = -1.13x + 481$, $R^2 = 0.99$. Some solvents are shown next to the data points.

The polarities of hexane, cyclohexane, and toluene are similar, but optical behaviors of their MEH-PPV solutions are very different. The results obtained from toluene, pyridine, and chloroform solutions also do not show a relationship between solvent polarity and the effective conjugation length, as illustrated in Figure 2. The solubility, reflecting conformation of MEH-PPV, is sensitive to three parameters including polarity, aromaticity, and architecture of solvents. This suggests that polymer conformation is a dominant factor in controlling the photophysical change. This argument can explain the results of Zheng et al.²⁰ where the dielectric constant of solvents was suggested to have no correlation with conjugation length. Because of the unsystematic change of solvent architectures in their system, the photophysics of MEH-PPV are governed by multiple parameters. In the next section, we demonstrate how to manipulate the location of absorption and emission spectra of the MEH-PPV by tuning solvent polarity.

Using a series of linear alcohols as a solvent allows polarity to gradually increase with decreasing length of alkyl group whereas systematic change of their architectures is maintained. Absorption spectra of MEH-PPV in alcohols ranging from methanol to dodecanol are shown in Figure 1b. Increasing polarity of alcohol from dodecanol to methanol causes the solubility to gradually diminish. The spectrum of MEH-PPV in dodecanol shows a broad peak at ~ 475 nm. A systematic blue-shift is observed as the alcohol polarity increases. The MEH-PPV in methanol exhibits an absorption peak at ~ 445 nm. The plot of absorption peak (λ_{max}) as a function of a

**Figure 3.** Absorption spectra of unfiltered solution of MEH-PPV in decanol as a function of temperature. Spectrum of the filtered solution is included for comparison. (inset) Absorption spectra of MEH-PPV in (solid line) chloroform and (symbol) mixture of chloroform (20% v/v) + decanol (80% v/v).

dielectric constant of alcohols is illustrated in Figure 2 where a linear relationship is observed. The spectra of methanol and ethanol solutions are similar to that of the hexane and cyclohexane solutions. The resemblance is in terms of position and pattern, which indicate a minor dependency of dipolar interaction between solvent and MEH-PPV on its photophysics.

Since the poor solvents dissolve part of powder sample, the molecular weight distribution and chemical structure of MEH-PPV due to the presence of tetrahedral defects could be different from that of the good solvents. However, the conjugation length should have a minor molecular weight dependency as discussed earlier. A series of experiments were also performed on each particular alcohol solution to further confirm that optical properties of MEH-PPV in the soluble fraction are not different from the whole sample. Solutions of MEH-PPV in alcohols were prepared by a serial dilution without filtration to preserve all polymeric molecules. Absorption spectra of these solutions have quite different structure compared to Figure 1b, as illustrated by a spectrum of MEH-PPV in decanol (Figure 3). At room temperature it exhibits a peak at 485 nm with a shoulder near 560 nm. The pattern resembles the spectra of aggregates induced by solvent-nonsolvent system reported in the literature^{25,27} and also illustrated in this study. The inset in Figure 3 shows absorption spectra of isolated MEH-PPV chain in chloroform and its aggregates in mixture of chloroform (20% v/v) and decanol (80% v/v). Clearly, aggregates and isolated chains of MEH-PPV exist in the unfiltered solutions. Varying concentration from 0.1 to 0.006 mg/mL does not affect the shape of the spectrum, indicating strong interchain interactions within the aggregates. An investigation into the details of the aggregation behavior of MEH-PPV in alcohols is currently being carried out in our laboratory. To measure optical properties of the isolated chains, the solution was heated to 90 °C, causing the dissociation of aggregates.^{7,30} Absorption spectra at elevated temperatures show the decrease of aggregate shoulder at 560 nm while the peak shifts to 470 nm. At 90 °C the solution contains only a fraction of aggregates, allowing measurement of spectrum of mostly isolated chains. The spectrum at 90 °C matches the spectrum of the filtered solution quite well (see Figure 3), indicating the same electronic properties of MEH-PPV chains in both solutions. Similar experiments on solutions of MEH-PPV in butanol and hexanol show the same results.

A control over conjugation length of MEH-PPV can also be achieved by using mixtures of good and poor solvents. Aggregation of isolated polymeric chains usually takes place

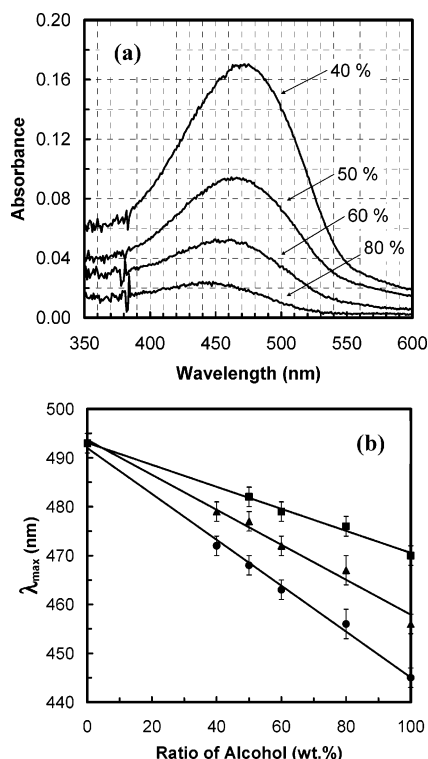


Figure 4. (a) Absorption spectra of saturated solutions of MEH-PPV in mixtures of methanol and chloroform. Ratios of alcohol in wt % are indicated by arrows next to the spectra. (b) Plots of peak position (λ_{\max}) as a function of alcohol ratio; (circle) chloroform + methanol, (triangular) chloroform + propanol, (square) chloroform + octanol. Solid lines are fitted to linear equations.

upon adding a poor solvent into MEH-PPV solution in good solvents.²⁵ At a relatively high concentration of 0.05 mg/mL the aggregates can be induced to form colloidal particles, which eventually precipitate, by keeping the solution in a refrigerator ($\sim 4^\circ\text{C}$) for about 24 h. The top portion is a clear solution saturated by majority of the isolated chains. Figure 4a shows spectra of the saturated solutions of MEH-PPV in mixtures of chloroform and methanol. Simultaneous decrease of λ_{\max} and absorbance with increasing ratio of the poor solvent is observed. This indicates parallel decrease of the effective conjugation length and solubility. Using mixtures of chloroform with other alcohols provides a similar trend. Figure 4b shows the linear relationship between peak position (λ_{\max}) and ratio of the poor solvents.

Evidence of Two Emitters in Isolated Collapsed Chain.

The shift of photoluminescence (PL) spectra of MEH-PPV in different solvents is parallel to that of the absorption spectra (see Table 1). PL spectroscopy provides additional information about the electronic properties of chromophore. In chloroform, toluene, and pyridine the patterns of emission and excitation spectra of MEH-PPV are similar, consistent with results in the literature.^{25–27} The spectra of MEH-PPV in toluene are illustrated in Figure 5a. The emission spectra consist of a peak at 560 nm with shoulder near 610 nm, corresponding to the relaxation of excited π -electrons to different vibrational energy levels at the electronic ground state.¹⁶ Besides the change of absolute intensity, the pattern is independent of excitation wavelength. The excitation profile detected at different wavelengths of emission spectrum also behaves accordingly, indicating the presence of only one type of emitter in the conjugated chains.^{16,17} Despite the nature of the conjugated chain which consists of multiple chromophores with various conjugation lengths, the fluorescence spectra often reflect the properties of

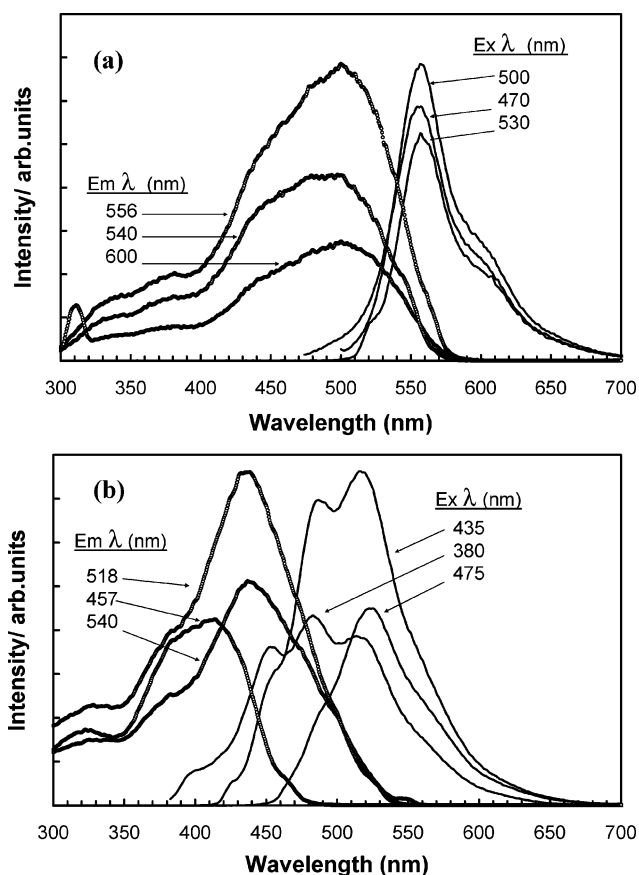


Figure 5. Excitation spectra (symbols) and emission spectra (solid lines) of MEH-PPV in (a) toluene and (b) cyclohexane measured at different emission wavelengths ($\text{Em } \lambda$) and excitation wavelengths ($\text{Ex } \lambda$), respectively.

the chromophores with the lowest transition energy gap. It is well-known that the shorter conjugation length segments can efficiently transfer energy to the neighboring longer conjugated segments prior to the emission.^{10,36,37}

Distinct behavior of the chromophores of MEH-PPV is detected in the poor solvents. Excitation and emission spectra of MEH-PPV in methanol, ethanol, hexane, and cyclohexane show several peaks that are not present in the good solvents. Figure 5b illustrates spectra of MEH-PPV in cyclohexane. It is obvious that structure of the emission spectra varies with the excitation wavelength. Using excitation energy near maximum absorption ($\text{Ex } \lambda = 435\text{ nm}$) yields emission spectra with two major peaks at 489 and 519 nm. A small shoulder at 455 nm becomes prominent when shorter excitation wavelength is used. On the other hand, increasing excitation wavelength results in the suppression of peaks at 455 and 489 nm while the intensity of the peak at 519 nm increases. Using excitation wavelength higher than 480 nm eliminates the two peaks at short wavelength, yielding a spectrum with peak and shoulder at 525 and 560 nm, respectively. The dependency of the emission pattern on excitation wavelength suggests that there are at least two distributions of electronic species with distinct ground- and excited-state properties.¹⁶ They absorb and emit photons at different energy regions. This is confirmed by measuring excitation profile at different emission wavelengths. As expected, the excitation profile can be separated into two patterns. The one measured at the first emission peak of 457 nm exhibits a broad peak center at about 400 nm. It does not absorb photon at wavelength above 480 nm. Another excitation profile measured at the low-energy tail of emission spectra shows a

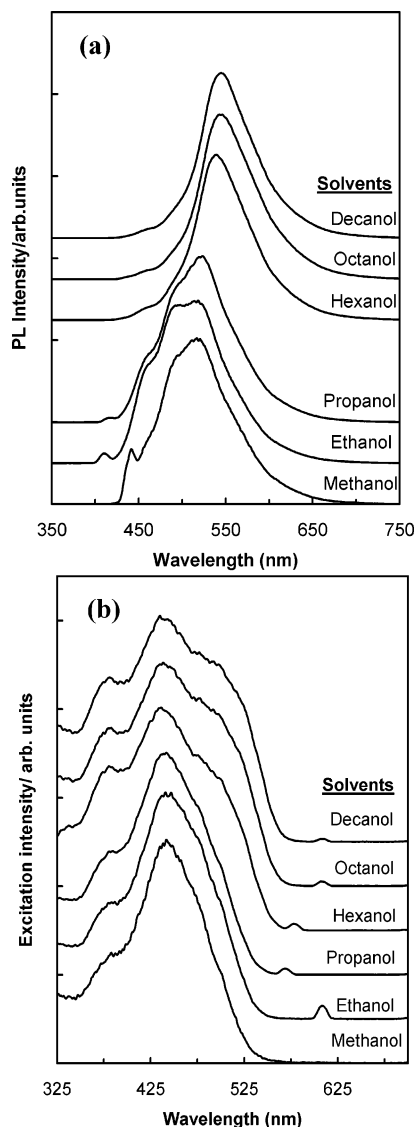


Figure 6. (a) Emission spectra of MEH-PPV in alcohols. The excitation wavelengths are selected at maximum absorption shown in Figure 1b ranging from 445 nm in methanol to 470 nm in decanol. (b) Excitation spectra of MEH-PPV in alcohols measured at emission wavelengths at peak of the emission spectra in (a).

sharp peak at 440 nm. This one absorbs photons with wide range of wavelength up to about 540 nm.

Origins of the two distributions of electronic species of MEH-PPV detected in the poor solvents are attributed to the increase of disorder in the collapsed conformation. The energy transfer along the conjugated backbone is known to be significantly suppressed when the conformational order of MEH-PPV segments is destroyed due to the collapse of chain and the increase of tetrahedral defects.^{36,37} It was reported that MEH-PPVs with more than 45 mol % of tetrahedral defects exhibited separate emission from individual chromophores with various conjugation lengths.³⁷ In poor solvents, the extreme collapse of polymeric chain introduces high fraction of the physical defects along the backbone and increases the disorder of segments. Therefore, the energy migration along the conjugated backbone is significantly decreased in the collapsed chain, allowing the emission from multiple chromophores to take place.

To further explore the origin of the separate emission of multiple chromophores, we investigate evolution of MEH-PPV spectra in the alcohols where a small step of chain expansion takes place. Figure 6a illustrates their emission spectra measured

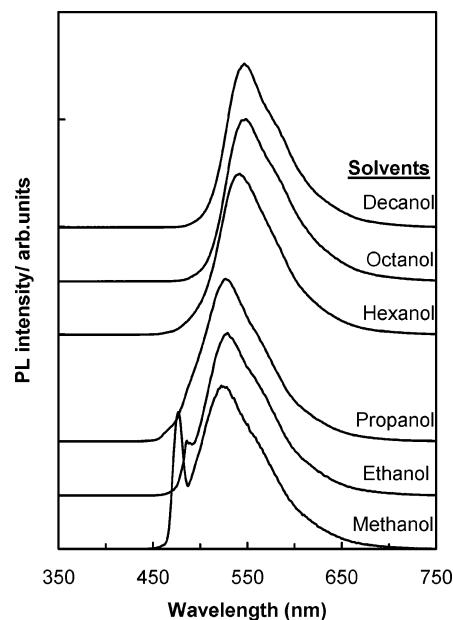


Figure 7. Emission spectra of MEH-PPV in alcohols. The excitation wavelengths are selected near the low-energy edge of the excitation profile, ranging from 500 to 550 nm.

by using excitation wavelength at maximum absorption (λ_{max}). The emission intensity of peaks at 455 and 485 nm varies upon expansion of the polymeric chain. The spectra of MEH-PPV in methanol, ethanol, propanol, and butanol clearly show these peaks while the solutions in hexanol, octanol, decanol, and dodecanol contain only a small fraction. The polymer coil in the latter group of alcohols probably expands enough to reduce a number of physical defects, allowing efficient energy migration along the backbone.³⁷ Excitation profiles of these solutions exhibit a red shift upon the expansion of chain (Figure 6b). They also exhibit a step pattern in which an equal step size of peaks relating to vibrational energy gap of the excited state is ~ 60 nm. The detection of vibronic structure probably arises from the decrease of segmental dynamics in the collapsed coils. The expansion of coils does not affect this gap but allows new transition to lower energy level as indicated by the growth of shoulder at higher wavelength.

Emission spectra of the chromophore with longer conjugation length can be extracted from the combined pattern in Figure 6a by selecting excitation wavelength above 500 nm. At this low-energy region the other electronic species does not absorb any photons. The spectra are shown in Figure 7. Sharp peaks at a short wavelength are attributed to the scattering of incident photons. The overall pattern is similar to that of the good solvent. Its shoulder, however, appears to be much broader. The spectrum of the methanol solution shows a peak at 525 nm. A red shift by about 25 nm occurs in the decanol solution in accordance with their absorption spectra.

A study of time-resolved fluorescence of MEH-PPV in a collapsed conformation supports the presence of two emitters. Figure 8 illustrates fluorescence decay profile of MEH-PPV in methanol. An attempt to fit the data to a single-exponential fails to provide a good fit. The fitting to double exponential, however, provides excellent fit with χ^2 value less than 1. Two lifetimes extracted from the fitting are 0.62 and 1.33 ns with ratio component of 0.46 and 0.54, respectively. Fluorescence decay of single emitter of MEH-PPV in chloroform²⁷ and chlorobenzene¹⁶ allows best fit to single exponential with lifetime of about 0.3 ns. Therefore, the detection of two lifetimes suggests the presence of two emitters.

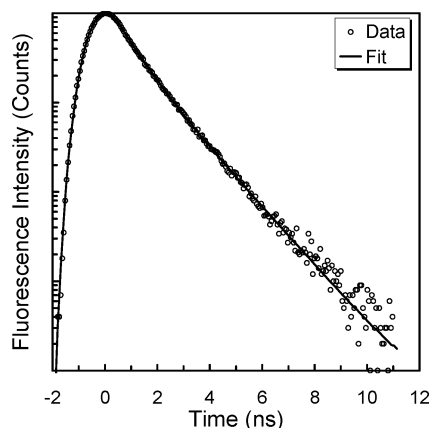


Figure 8. Time-resolved PL of MEH-PPV in methanol using excitation wavelength at 450 nm and monitored at 510 nm. Symbol is data, and solid line is fitted to double exponential.

Effect of Temperature on Photophysics. Increasing temperature normally causes expansion of polymer coil. However, it also promotes intramolecular dynamics. Variable-temperature studies of MEH-PPV^{14,20,41} and other conjugated polymers^{13,30} have observed a blue-shift of emission spectra accompanied by a decrease of quantum yield upon increasing temperature. This behavior is typically attributed to conformational change of polymer chain and a fluctuation of dielectric constant of solvent.^{13,14} Our study further investigates the effect of local chain confinement on photophysical response to temperature change. This will shed more light on mechanism of this temperature-dependent behavior. In this system, solutions contain mostly isolated chains while aggregated species are present in the previous investigation.¹⁴ Therefore, our results show some discrepancies compared to their study.

Figure 9 illustrates absorption and emission spectra of MEH-PPV dissolved in various solvents as a function of temperature. The extent of chain collapse increases from pyridine to decanol and butanol. A blue-shift accompanied by a decrease of emission intensity upon increasing temperature is observed. This thermal reversible behavior is detected from the corresponding absorption spectra. We did not detect an increase of the emission intensity in any solutions, which differs from the previous report.¹⁴ Increasing temperature involves dissociation of aggregates in their system whereas its effect is limited to intrinsic nature of chromophores of isolated chains in our system. The simultaneous decrease of absorbance and emission intensity indicates that the increase of temperature causes the decrease of population in both electronic ground and excited states of chromophores with relatively long conjugation length.

The blue-shift of spectra occurs at different rates depending on the magnitude of local chain confinement. Figure 10 shows peak position of MEH-PPV spectra in various solvents as a function of temperature. A linear relationship between λ_{max} and temperature is observed from all solutions consistent with studies of other conjugated polymers.¹³ Equations obtained from linear regression are listed in the figure caption. Although fittings of absorption and emission data do not provide the exact same results, they still exhibit the same trend. The emission spectra should provide more reliable results though because it constitutes of much sharper peaks. For the extended chains in chloroform, rate of the blue shift, which is 0.290 nm/K, is found to be highest. The rate of the spectra shift is found to systematically decrease with increasing magnitude of the local chain confinement, ranging from MEH-PPV solutions in chloroform,

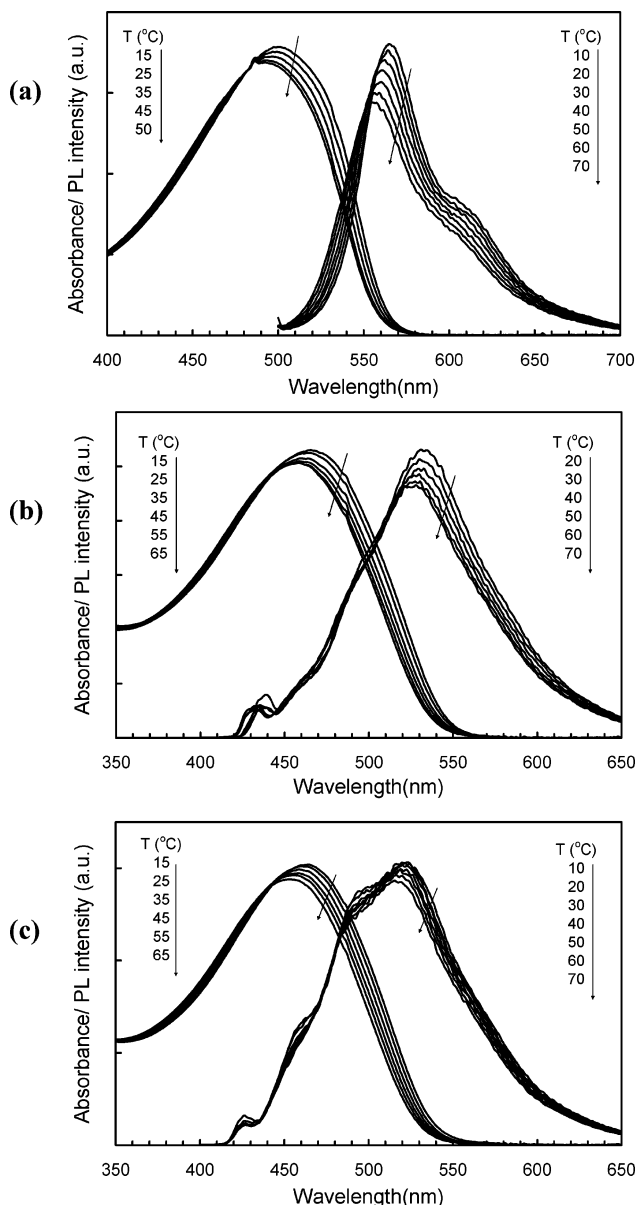


Figure 9. Absorption and emission spectra of MEH-PPV solutions in (a) pyridine, (b) decanol, and (c) butanol measured as a function of temperature. Excitation wavelength for the measurement of emission spectra was selected at peak of their absorption spectra.

toluene, pyridine, decanol, butanol, and cyclohexane. For the most confined chain in cyclohexane, emission spectra shift at a rate of 0.137 nm/K. This rate is slightly higher than that of the decanol and butanol solution. This is found to be due to the present of multiple emitters in the collapsed chain. Its overlapped emission spectra obscure the determination of λ_{max} . To eliminate this interference, excitation wavelength at 510 nm is used. Rates of the blue-shift are 0.100 nm/K for all solutions in the poor solvents. The effect of local chain confinement on the diminishing rate of absorbance is parallel to the results of the blue-shift.

Planarization of phenyl rings is known to enhance the delocalization of π -electrons within conjugated chains.²⁹ Our recent NMR study observes solvent-dependent rotational dynamics of the phenyl rings within MEH-PPV backbone.⁴⁰ This type of intrachain dynamics can destroy the approximately coplanar configuration of the phenyl rings within each chromophore. Therefore, we propose that the phenyl rotation is one important parameter, determining the systematic change of

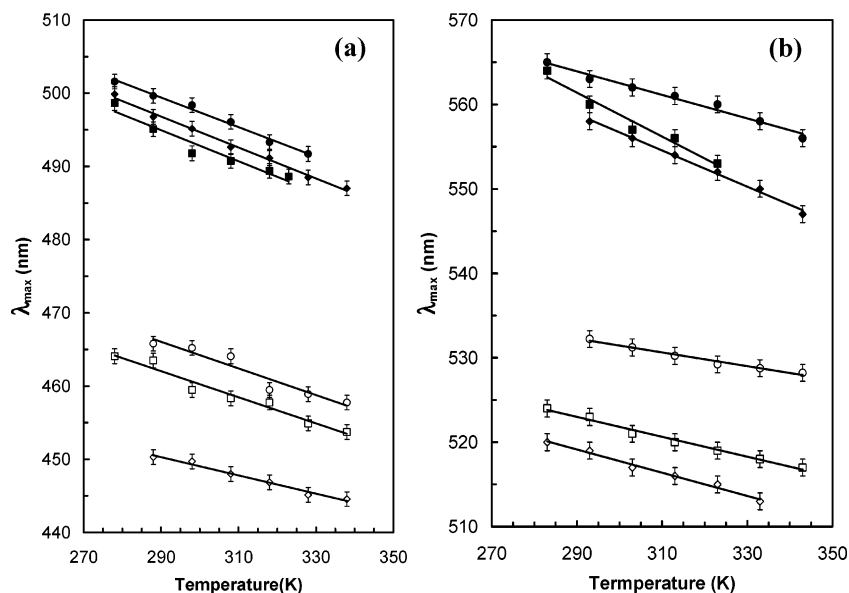


Figure 10. Plots of λ_{\max} of absorption (abs) and emission (em) spectra as a function of temperature. Solid lines are fitted to linear equations. Solvents: (■) chloroform; (abs) $y = -0.212x + 556$; (em) $y = -0.290x + 646$, (◆) toluene; (abs) $y = -0.211x + 556$; (em) $y = -0.214x + 621$, (●) pyridine; (abs) $y = -0.202x + 558$; (em) $y = -0.154x + 608$, (○) decanol; (abs) $y = -0.182x + 519$; (em) $y = -0.100x + 562$, (□) butanol; (abs) $y = -0.178x + 514$; (em) $y = -0.100x + 511$, (◇) cyclohexane; (abs) $y = -0.125x + 486$; (em) $y = -0.137x + 558$.

optical properties as a function of temperature. The increase of the rotational rate at elevated temperature could effectively reduce molar absorption coefficient of conjugated chain. The chromophore with relatively long conjugation length should feel the effect first because it requires larger number of phenyl rings to arrange in coplanar fashion. Extended conformation of MEH-PPV in chloroform allows the rotational process to take place quite freely.⁴⁰ The decrease rate of λ_{\max} and absorbance and emission intensity upon increasing temperature is therefore found to be highest. An increase of local chain confinement in collapsed chains limits the response of rotational dynamics upon increasing temperature. This explains a systematic decrease of the rate of blue-shift with increasing magnitude of local chain confinement.

Conclusions

We have shown that photophysics of MEH-PPV closely relate to its conformation, which can be finely tuned by controlling polymer-solvent interactions. The quality of solvent depends on various parameters including molecular architecture, aromaticity, and polarity. A good solvent such as chloroform allows polymer chains to adopt an extended conformation, resulting in the increase of effective conjugation length. In poor solvents such as aliphatic alkanes and alkyl alcohols chains collapse, resulting in the decrease of conjugation length possibly due to the presence of higher number of physical defects. Separate emission of chromophores with various conjugation lengths is detected in the collapsed coils, possibly due to the suppression of energy migration along conjugated backbone. Variable temperature studies observe a decrease of λ_{\max} and absorbance and emission intensity of MEH-PPV spectra upon increasing temperature. The decreasing rate is found to depend on magnitude of local chain confinement. Phenyl ring rotation is proposed to be one important parameter responsible for this behavior.

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