CHAPTER IV
VERSATILE ROUTE FOR TUNING OPTICAL PROPERTIES OF POLY(2-METHOXY-5-(2'-ETHYLHEXYLOXY)-1,4-PHENYLENEVINYLENE) (MEH-PPV)

4.1 Abstract

In the present contribution, we report a versatile method for tuning optical properties of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) in its solution with 1,2-dichloroethane, accomplished by reacting with pyridinium formate (PF), a volatile organic salt. We can systematically control the position of absorption and photoluminescent (PL) spectra of MEH-PPV by adjusting the concentration of PF in the solution. The addition of 10 vol.-% PF caused a blue-shift in the absorption spectra by about 65 nm. When the concentration of PF decreased to 0.1 vol.-%, the blue-shift occurred to a lesser extent, about 25 nm. The measurements of PL spectra showed similar behaviors. The λ_{max} shifted from 558 nm to 546 and 552 nm when 10 vol.-% and 0.1 vol.-% of PF were added, respectively. The changes of PL colors from orange to yellow and green, respectively, were observed by naked eyes. Structural investigation by nuclear magnetic resonance and Fourier-transformed infrared spectroscopy indicated that the changes of the optical properties were due to chemical modifications along the main chain and the side groups of MEH-PPV. These results implied a simple route for engineering the HOMO-LUMO energy gap of MEH-PPV, which could be utilized in advanced applications such as organic light emitting devices and solar cells.

(**Key-words**: MEH-PPV; Photophysics; Photoluminescence; Tuning of optical properties)

4.2 Introduction

Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) is one of the well-known conjugated polymers with many interesting physical properties, such as photoconductivity[1,2] and high luminescence efficiency in both photo- and electroluminescence.[3,4] It, therefore, holds great promises in various electronic applications, such as organic light-emitting diodes (OLED),[5-7] sensors[8-10] and solar cells.[11,12] In the past few decades, many researchers have investigated detailed properties of conjugated polymers in order to understand their fundamental behaviors. In general, the intrinsic nature of conjugated polymers derives mainly from their architectures consisting of alternating single and double/triple bonds along the main chain. The appropriate arrangement of π-orbitals in the backbone could provide a convenient pathway for π-electrons to delocalize over the entire molecule. However, this ideal situation is never realized because of the flexibility of the polymer chain. The delocalization of the π-electrons is normally confined within some distances, called conjugation lengths. Various chromophores with different conjugation lengths exist in one conjugated chain.[13,14] Therefore, its electronic properties are dictated by the distribution of chromophores within the system.[15-17]

One of the challenges for developing conjugated polymers is the tuning of their electronic and optical properties, which are necessary for specific applications. This includes, for example, the engineering of colors to obtain a full range of spectrum in OLED and the manipulation of HOMO-LUMO energy levels in solar cells. The methods for tuning the properties of conjugated polymers generally involve the synthesis of new macromolecules[18-21] or the modification of the chemical structure of the existing conjugated polymers.[22-26] MEH-PPV is an example of a modified chemical structure of polyphenylenevinylene-based conjugated polymers. The incorporation of the flexible MEH side groups increases the solubility of this polymer in a common solvent, which, in turn, facilitates its fabrication into thin films. The bulkiness of the MEH side groups also reduces the segmental aggregation of the main chain, an important factor that affects its photoemission color and efficiency.[27-29] Furthermore, the phenyl rings along the

MEH-PPV backbone become more difficult to rotate around single bonds, resulting in the extension of conjugation lengths.

It has been shown that the tuning of optical properties of conjugated polymers can also be achieved via polymer-polymer blending approach.[30-34] Although the procedure is quite simple, this method does not modify the HOMO-LUMO energy levels of each polymer in the blend. The photo- and electroluminescence spectra always constitute of multiple regions, contributed from simultaneous emitting of different luminophores in the system.[30,32,33] The manipulation of the emitting colors can be done by simply adjusting the ratio of the blend and the extent of energy transfer. Furthermore, the polymer-polymer blends tend to exhibit micro- and nano-phase separation due to the immiscibility of the components, which, in turn, leads to inhomogeneity in local properties.[31-34] The issue of phase separation can be overcome by a copolymerization approach.[35-37] The structural change of luminophores in copolymers allows for a direct engineering of HOMO-LUMO energy levels, which yields narrow photo- and electroluminescence spectra. However, the copolymerization is normally a multi-step process, which requires complicated procedures and expensive catalysts/chemicals. Therefore, it is important to seek a simple and cheap method for chemically modifying conjugated polymers that provides an easy control over their optical properties.

In a recent study by some of us, fibers of MEH-PPV were electrospun from its solutions in 1,2-dichloroethane (DCE) with polystyrene being used as the fiber-forming template and pyridinium formate (PF), a volatile organic salt, being used as the conductivity modifier. It was accidentally observed that the solutions changed their color from orange to yellow after being aged at ambient conditions for 1 month.[38] It was postulated, based on the infrared spectroscopic result, that partial decomposition of MEH side groups (~15%) was responsible for this observation. We envisioned that such a side chain decomposition induced by the addition of PF could be a simple approach to modify the chemical configuration of MEH-PPV, resulting in the chemical structure that resembles that of a random copolymer between PPV and MEH-PPV. Despite such an implication, a detailed study on any structural change that affects the change in the color of MEH-PPV in the presence of PF based

on a more direct method, such as nuclear magnetic resonance spectroscopy (NMR), is necessary to gain an insight into the color-changing process of this polymer.

In the present study, we performed systematic experiments to investigate the photophysical change of MEH-PPV solutions in DCE in the presence of PF, which could lead to a simple procedure for controlling the electronic properties of this polymer. Effects of concentrations of MEH-PPV and PF were investigated. The changes in the absorption and the photoemission spectra were followed as a function of time. Fourier-transformed infrared spectroscopy (FT-IR) and NMR were used to characterize the structural change of MEH-PPV in the system.

4.3 Experimental

4.3.1 Materials

The MEH-PPV used in this study was synthesized according to the procedure described in literature.[26] All solvents purchased from different sources (Carlo Erba and Merck) were analytical grade.

4.3.2 Preparation of Solutions

Fresh solutions of MEH-PPV (0.001, 0.005 and 0.01% w/v) were prepared by dissolving measured amounts of the polymer powder in DCE. Different concentrations (0.1 and 10 vol.-%) of PF, prepared by mixing pyridine and formic acid in an equimolar quantity, were then added into the system. The mixed solutions were sealed in vials and left in darkness at ambient conditions. Absorption and photoemission spectra of the solutions were recorded as a function of time until no noticeable change was observed.

4.3.3 Characterizations

The absorption spectra were measured using a Hewlett-Packard 8254A diode array UV-vis spectrophotometer. Quartz cuvettes with thicknesses of 2 mm or 10 mm, depending on the polymer concentration, were used. The emission spectra were measured using a Perkin-Elmer LS50 luminescence spectrometer. An inner filter effect was minimized by using a 2 mm-thick quartz cuvette in all

measurements. Any structural change of MEH-PPV was investigated by a Bruker Avance-AC400 proton-nuclear magnetic resonance spectroscopy (^{1}H-NMR), operating at 400 MHz, and a Thermo-Nicolet Nexus 670 Fourier-transform infrared spectrometer (FT-IR). Samples for these measurements were prepared by evaporating the solvent at 130 °C for 1 h. Only small amount of the solvent remained after this procedure. The samples were subsequently dried at 80 °C in a vacuum oven for 12 h. Solutions of MEH-PPV in DCE and PF in DCE were also subjected to the same drying procedure. These were used as control samples.

4.4 Results and discussion

4.4.1 Absorption Study

In the first section, we investigated the variation in the absorption spectra as a function of the reaction time, which reflects the photophysical changes of MEH-PPV chromophores in ground state. Figure 4.1 illustrates the results obtained from the system of 0.01 % w/v MEH-PPV solution containing 10 vol.% PF. The spectrum of the freshly-prepared solution (0 day) exhibits a broad pattern with the maximum absorption (λ_{max}) at about 500 nm. The broadness of the spectrum arises from an intrinsic nature of the conjugated chain, which consists of various chromophores with different conjugation lengths.[14,17] Therefore, the shape of the whole spectrum envelops all possible electronic transitions, which take place at different wavelengths, depending on HOMO-LUMO energy gaps of each particular chromophore.

The pattern of the absorption spectrum changes significantly upon aging in ambient conditions for 1 day. Its absorbance markedly drops while the λ_{max} shifts to a higher energy region. Increasing the reaction time to 2 days causes a blue-shift of the spectrum by about 30 nm. We also observe the increase in the absorbance at the high-energy region (λ < 450 nm), while the absorbance at the low-energy region simultaneously decreases. The progress of reaction continues up to about 14 days. Increasing the reaction time further to 37 days hardly affects the pattern of the absorption spectrum, suggesting the completion of this process. The solution of the

final product exhibits λ_{max} at about 434 nm, while the absorbance drops by about 55% compared to that of the original solution. In addition, the pattern of the spectrum appears much broader with the high-energy region becoming wider. The blue-shift of the absorption spectra corresponds to the widening of HOMO-LUMO energy gap of the modified MEH-PPV. In other words, long chromophores are converted to shorter ones upon the reaction with PF. In addition, the decrease of the absorbance indicates the lowering of the molar absorption coefficient.
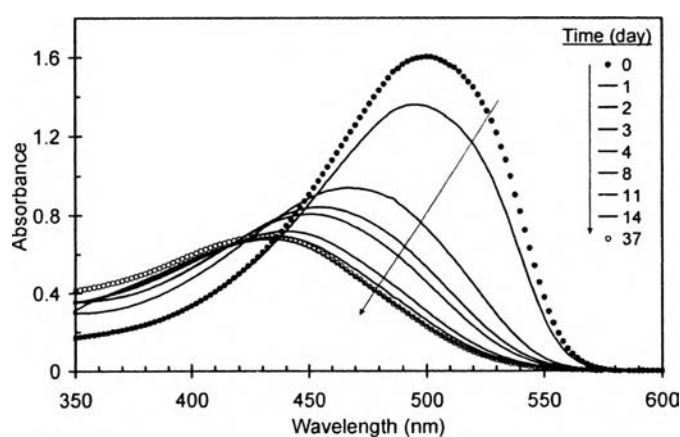
Figure 4.1 Absorption spectra of 0.01% (w/v) MEH-PPV in 1,2-dichloroethane (DCE) with the addition of 10 vol.-% pyridinium formate (PF) measured as a function of reaction time. Arrow indicates the change in the spectra with increasing the reaction time.

We carried out additional experiments to explore other parameters that affected the progress of the reaction. The solutions of MEH-PPV at various concentrations [e.g., 0.001, 0.005 and 0.01% (w/v)] were prepared while the PF content was kept constant at 10 vol.-%. All solutions exhibit the blue-shift in the absorption spectra and the decrease in the absorbance with increasing the reaction time. Plots of λ_{max} and the absorbance as a function of time are shown in Figure 4.2(a) and (b). The rate of the reaction is found to increase with a decrease in the concentration of MEH-PPV (or with an increase in the PF to MEH-PPV ratio). The reactions of 0.001, 0.005 and 0.01% (w/v) solutions are completed after the solutions having been aged for 8, 11 and 14 days, respectively. Despite that, the λ_{max} of the

final products is detected at practically the same location ($\lambda_{max} \sim 434$ nm). The change in the absorbance shows a consistent trend. These observations indicate that the concentration of the added PF is an important parameter for controlling the HOMO-LUMO energy gap of the modified MEH-PPV.

As mentioned earlier, the broadness of the absorption spectra reflects the distribution of chromophores with various conjugation lengths in the conjugated backbone of MEH-PPV. One can follow the variation in the size distribution of chromophores by plotting the ratios between the integrated areas under two different energy regions of the absorption spectrum, i.e., [350-490 nm]/[490-600 nm], as illustrated in Figure 4.2(c). This ratio is about 1 for the original solutions of MEH-PPV. It gradually increases with an increase in the reaction time for all solutions. The rate of change is highest for the 0.001% (w/v) solution, which is consistent with the variation of λ_{max} and the absorbance. The ratios of the integrated areas reach the value of about 8 after the completion of the reaction, corresponding to the markedly increase in the high-energy chromophores in the system. We also observe that the final product of each solution exhibits slightly different values of the ratios.

In the next section, we performed similar experiments to investigate the effects of PF concentration. The solutions of MEH-PPV with concentrations of 0.001, 0.005 and 0.01% (w/v) were prepared while the quantity of PF was reduced from 10 to 0.1 vol.-%. Figure 4.3 illustrates the results obtained from the 0.01% (w/v) MEH-PPV solution with 0.1 vol.-% PF. It is obvious that the blue-shift and the decrease of the absorbance occur with increasing the reaction time. However, the rate of change is much slower as compared to the solution of 0.01% (w/v) MEH-PPV in the presence of 10 vol.-% PF. The absorption spectrum changes slightly after 4 days. The reaction yields the final product after 14 days and its absorption spectrum exhibits λ_{max} at ~476 nm. Previously, it was found that the solutions of MEH-PPV with 10 vol.-% PF showed the final products with λ_{max} of the absorption spectra at ~434 nm. These results indicate that the change in the PF concentration leads to the modified MEH-PPV with different optical properties. In other words, PF with different concentrations could be used to tune the peak position of the absorption spectrum or the conjugation length of chromophores of the conjugated polymer.
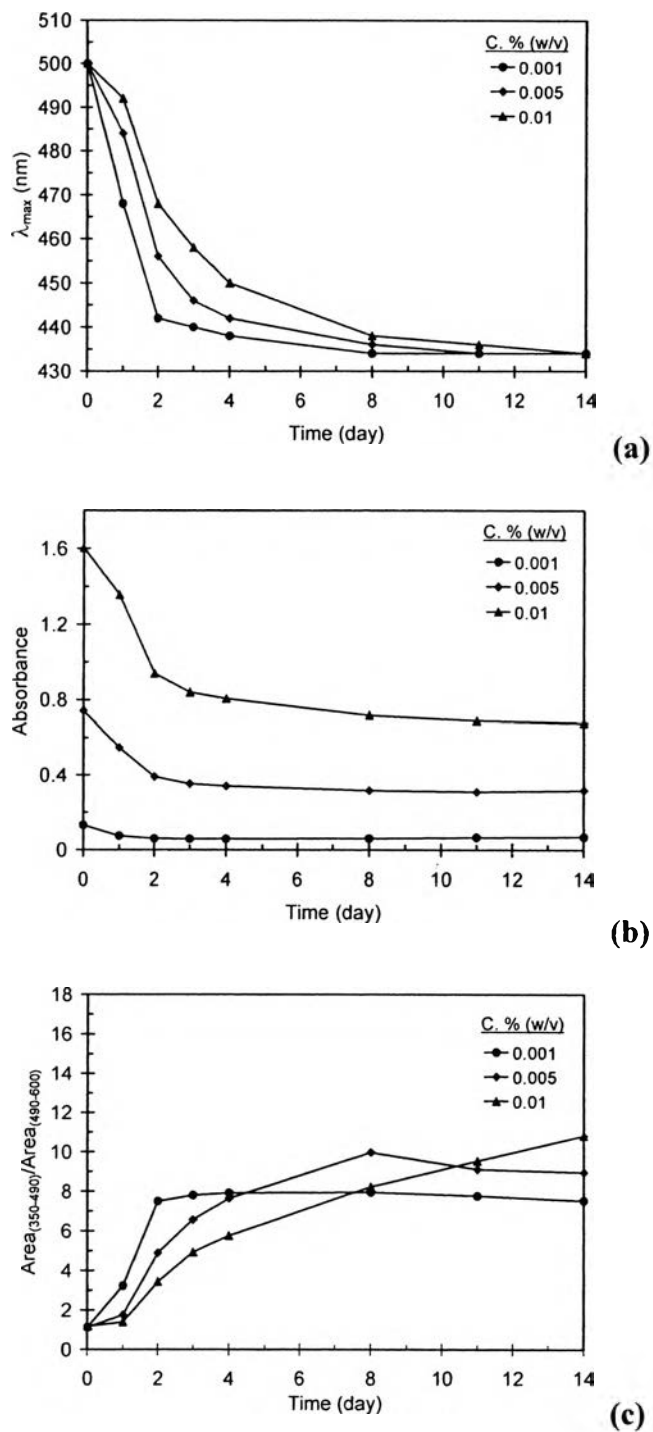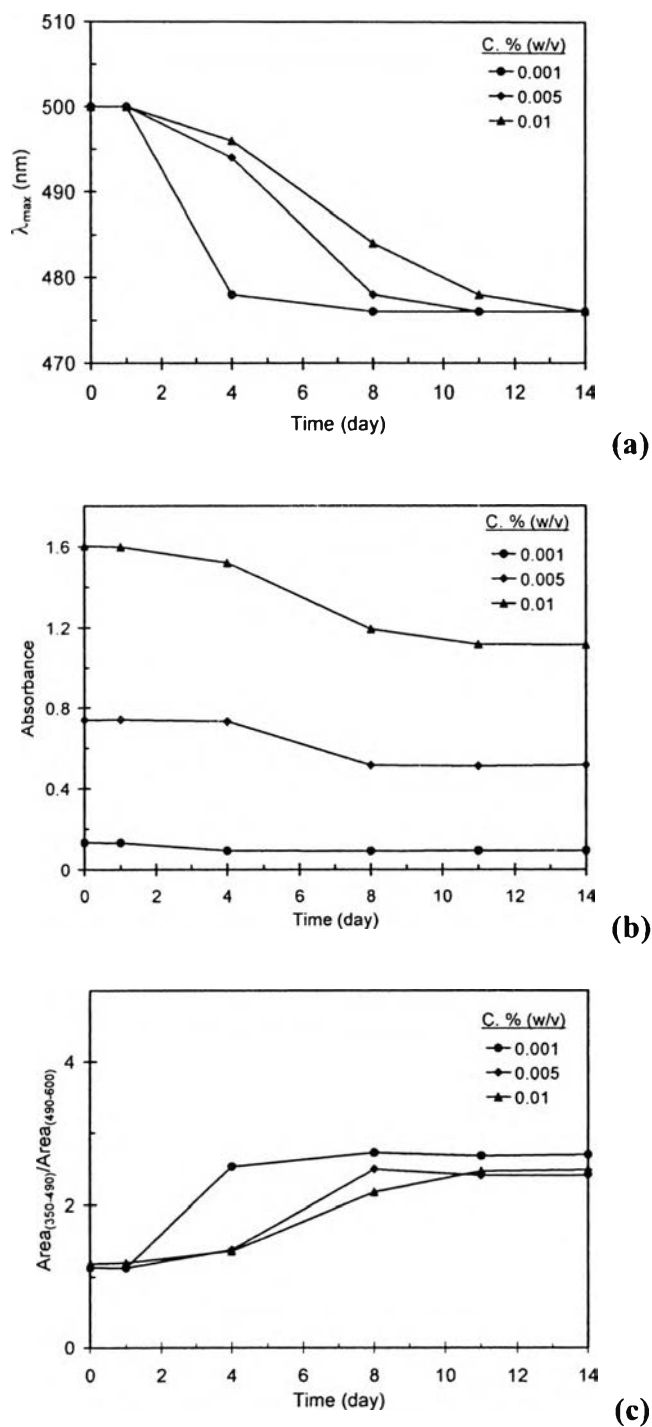
Figure 4.2 Plots of (a) λ_{max}, (b) absorbance and (c) $Area_{(350-490)}/Area_{(490-600)}$ of the absorption spectra of MEH-PPV at various concentrations in DCE with the addition of 10 vol.-% PF measured as a function of reaction time.
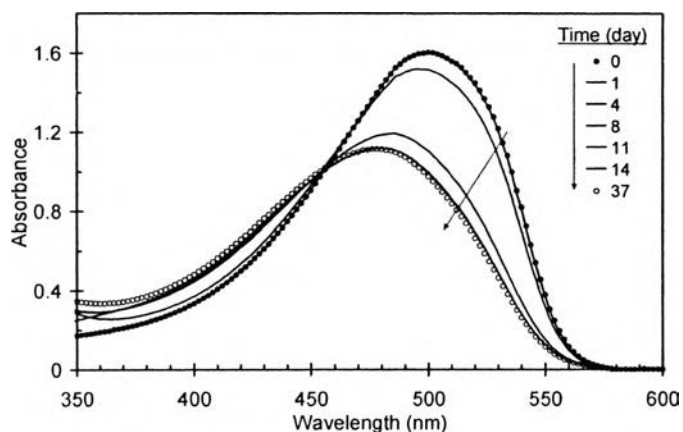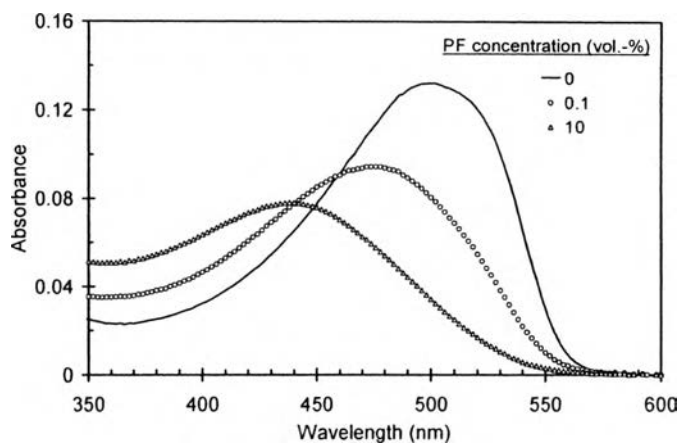
Figure 4.3 Absorption spectra of 0.01% (w/v) MEH-PPV in DCE with the addition of 0.10 vol.-% PF measured as a function of reaction time. Arrow indicates the change in the spectra with increasing the reaction time.

The results obtained from the solutions of 0.001 and 0.005% (w/v) with 0.1 vol.-% PF confirm our finding. The changes in the absorption spectra with increasing the reaction time are summarized in Figure 4.4. The λ_{max} of all the solutions decreases with increasing the reaction time and reaches a constant value at ~476 nm after 14 days. The variation in the absorbance shows similar results. Figure 4.4(c) shows the ratios between the integrated areas under two different energy regions of the absorption spectrum, i.e., [350-490 nm]/[490-600 nm], which shows the increase of the values by about 2 times. It is important to note that the MEH-PPV solutions with 10 vol.-% PF exhibit the change in this value by about 8 times. Therefore, the variation in the PF concentration can be used to tune the average conjugation length (λ_{max}), the molar absorption coefficient and the size distribution of chromophores in the modified MEH-PPV. The concentration of the polymer also affects the rate of the overall process. The experiments performed on both systems show the increase of the reaction rate with decreasing the polymer concentration (or with increasing the PF to MEH-PPV ratio). To summarize all results, we plot the absorption spectra of the final products obtained at two concentrations of the added PF as shown in Figure 4.5. The absorption spectrum of the original MEH-PPV solution with identical concentration is included for comparison.

Figure 4.4 Plots of (a) λ_{max}, (b) absorbance and (c) Area$_{(350-490)}$/Area$_{(490-600)}$ of the absorption spectra of MEH-PPV at various concentrations in DCE with the addition of 0.1 vol.-% PF measured as a function of reaction time.
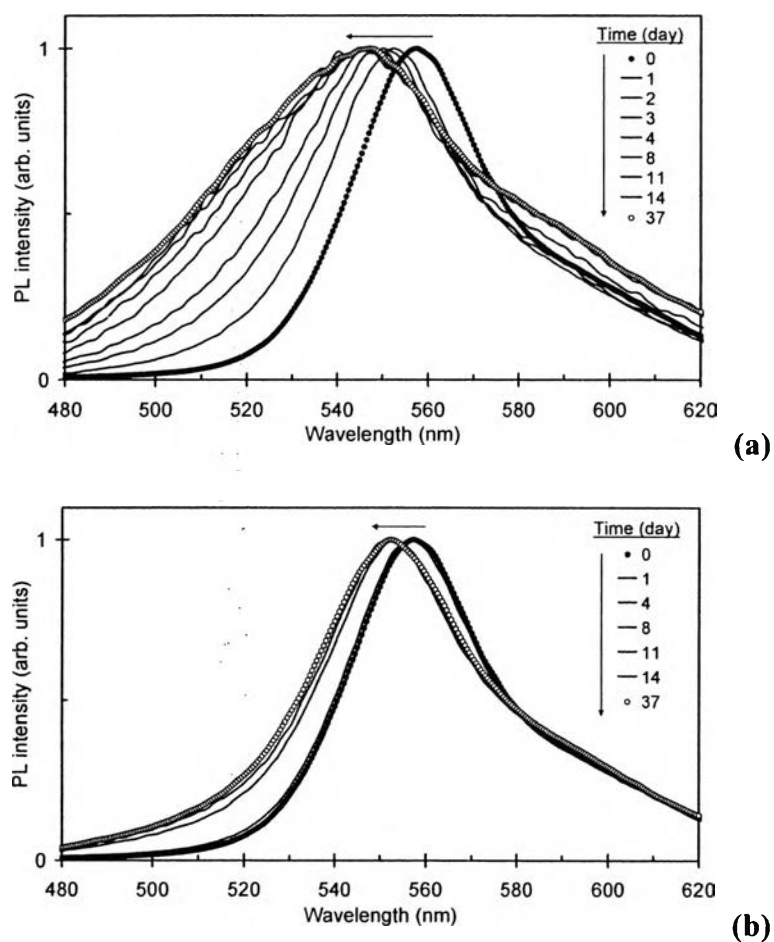
Figure 4.5 Absorption spectra of 0.001% (w/v) MEH-PPV in DCE at various concentrations of PF after having been aged for 37 days.

4.4.2 Emission Study

The results on photoluminescence show a similar behavior to that of the absorption, previously discussed. The results obtained from the systems of 0.01 % (w/v) MEH-PPV solutions with 10 and 0.1 vol.-% PF are respectively shown in Figure 4.6(a) and (b). All of the photoluminescent (PL) spectra were recorded with an excitation wavelength of 450 nm. The PL spectrum of the original MEH-PPV solution exhibits λ_{max} at about 559 nm along with a broad shoulder at about 590 nm. The spectra gradually shift to a high-energy region with an increase in the reaction time and become stable after 14 days. The products of MEH-PPV with 10 or 0.1 vol.-% PF exhibit the PL spectra with λ_{max} of ~546 nm and ~552 nm, respectively. The solutions appear green and yellow, respectively, under the illumination of a black light (λ ~ 385 nm). The experiments carried out on 0.005 and 0.001% (w/v) MEH-PPV solutions produced similar results. Figure 4.7 shows that λ_{max} as measured on all of the solutions investigated decreases with an increase in the reaction time. Similar to the behavior of the absorption spectra, the final values of λ_{max} are dictated by the PF concentration, while the rate of change increases with a decrease in the polymer concentration. Interestingly, the peak position of the PL spectra of the original MEH-PPV solutions slightly shifts to a low-energy region with increasing the polymer concentration. This corresponds to the inner-filter effect

in which the emitted photons with relatively high energy are re-absorbed by neighboring chromophores. Such an effect becomes dominant upon increasing the concentration of chromophores, causing the PL spectra to red-shift and the overall emission intensity to decrease.
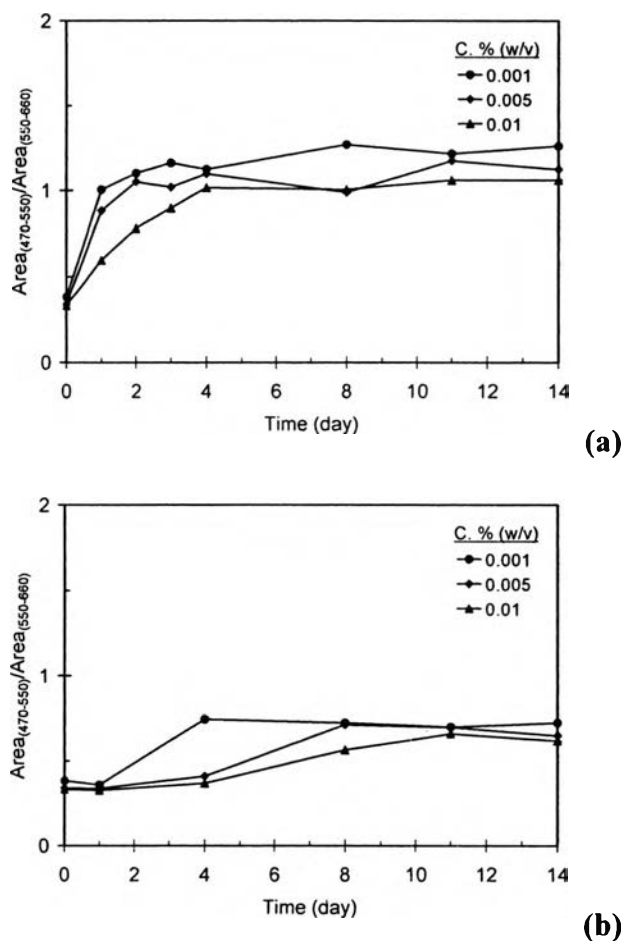

Figure 4.6 Emission spectra of 0.01% (w/v) MEH-PPV in DCE with the addition of (a) 10 or (b) 0.1 vol.-% PF measured as a function of reaction time. Arrow indicates the change in the spectra with increasing the reaction time. All spectra are normalized for clarity.

The PL spectra of the modified MEH-PPV which has been aged for 14 days exhibit a much broader shape compared to that of the original solution (see Figure 4.6(a)), which corresponds to the increase in the size distribution of chromophores in the systems. The ratios between the integrated areas under two

different energy regions of the PL spectrum, i.e., [470-550 nm]/[550-660 nm], of each solution are calculated and plotted in Figure 4.8(a) and (b). The ratio is about 0.4 for the original MEH-PPV solution. The value gradually increases with the reaction time, which corresponds to the conversion of the low-energy chromophores to the higher-energy ones. The ratios reach final values of about 1.1 and 0.6 for the systems containing 10 and 0.1 vol.-% PF, respectively.
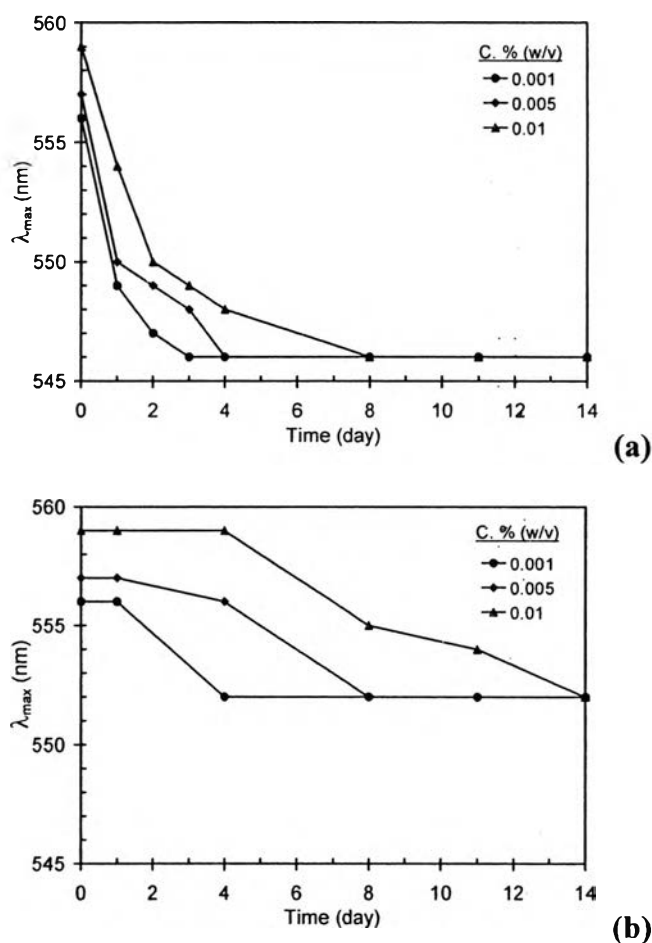
(a)

(b)

Figure 4.7 Plots of λ_{max} of the emission spectra of MEH-PPV at various concentrations in DCE with the addition of (a) 10 or (b) 0.1 vol.-% PF measured as a function of reaction time.

Figure 4.8 Area$_{(470-550)}$/Area$_{(550-660)}$ of the emission spectra of MEH-PPV at various concentrations in DCE with the addition of (a) 10 or (b) 0.1 vol.-% PF measured as a function of reaction time.

4.4.3 Chemical Structure Study

In the next section, NMR and FT-IR spectroscopy were used to investigate any change in the structure of MEH-PPV, upon coming into contact with PF, that might be responsible for the observed optical properties. Figure 4.9 displays ^{1}H-NMR spectra of the original MEH-PPV, PF and the modified MEH-PPV. The comparison between the spectra of PF and the modified MEH-PPV indicates that the organic salt is completely removed from our samples. The spectrum of the original MEH-PPV constitutes the peaks at 7.19 and 7.50 ppm, corresponding to olefinic and aromatic protons along the conjugated backbone.[39] The signals of methoxy and

alkoxy protons of the side groups are also detected at about 3.7 to 4.0 ppm. Series of new signals, as illustrated in Figure 4.9c, are detected when the MEH-PPV is reacted with 0.1 vol.-% PF. The intensity of these peaks becomes much more pronounced when the concentration of PF increases to 10 vol.-% (viz. the increase in the extent of the reaction). Some additional peaks are also observed (see Figure 4.9d). The appearance of these new peaks is accompanied by a simultaneous decrease in the intensity of the peaks at 7.19 and 7.50 ppm of the original MEH-PPV. In addition, the peaks of the side groups at ~4 ppm become much broader. The detection of new peaks near 5.6 and 8 ppm suggests the incorporation of formate (HCOO⁻) groups, probably by the addition reaction with reactive double bonds in the conjugated backbone. The peaks near 5 ppm suggest the existence of phenolic groups in the modified polymer, which is likely to be due to the breaking of ether groups of the side groups (see below). The peaks near 10 ppm also suggest the existence of aldehyde groups. However, it is not our intention to try to identify the exact origin of each peak, as one needs to carry out further experiments to follow the reaction.
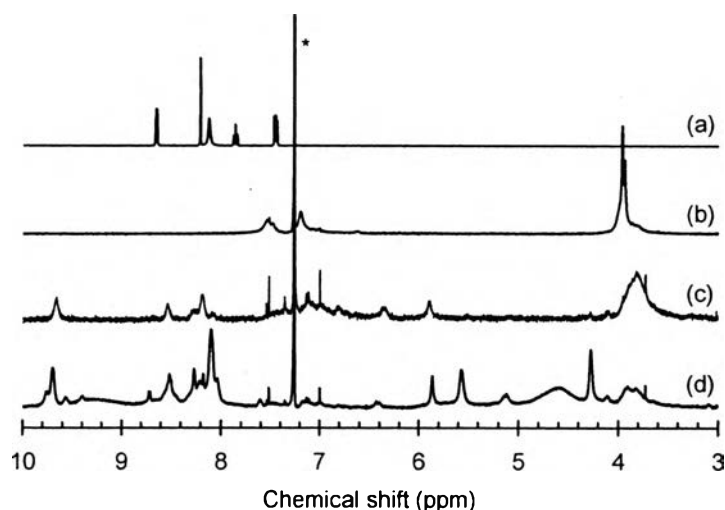
Figure 4.9 ^{1}H-NMR spectra of (a) PF, (b) the original MEH-PPV, (c) MEH-PPV that had been reacted with 0.1 vol.-% PF and (d) MEH-PPV that had been reacted with 10 vol.-% PF in d-chloroform. The solutions in (c) and (d) had been aged for 4 days prior to the removal of PF and solvent (see text). Peak marked with asterisk (*) is due to the residual solvent. For clarity of the presentation, peaks belonging to other protons of the alkyl side groups are not included.
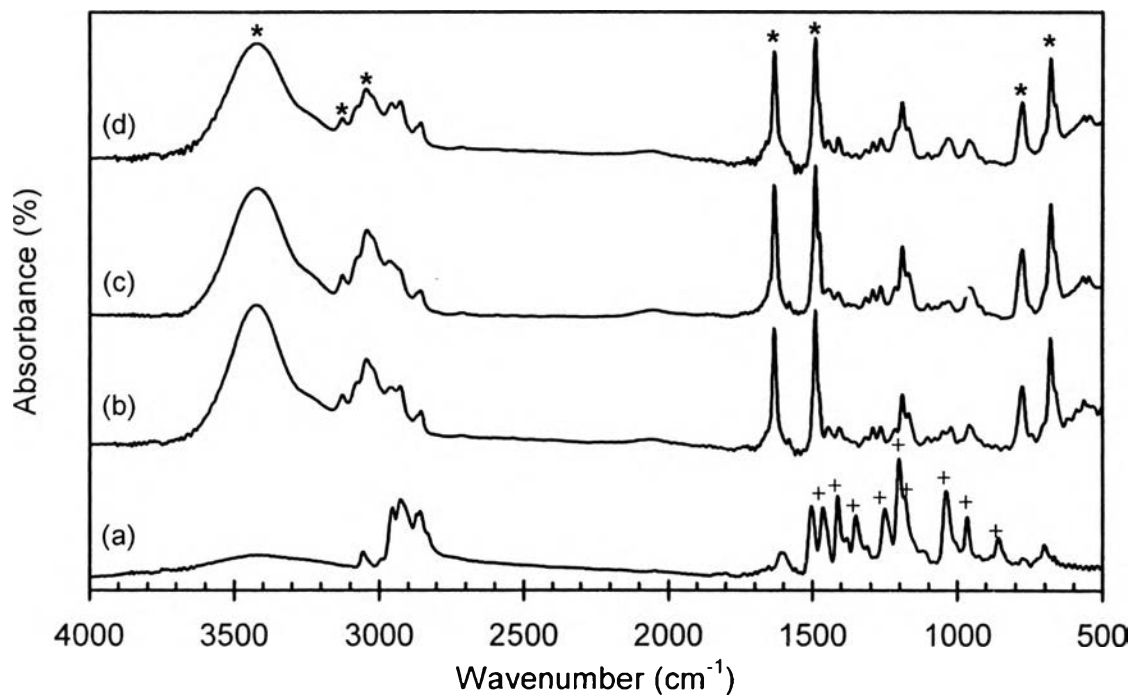
Figure 4.10 FT-IR spectra of (a) the original MEH-PPV and the modified MEH-PPV from (b) 0.001, (c) 0.005 or (d) 0.01% (w/v) MEH-PPV in DCE with the addition of 10 vol.-% PF. The solutions had been aged for 75 days prior to the removal of PF and solvent.

* = The intensity of the peak was greatly increased after PF addition.

\+ = The intensity of the peak was greatly decreased after PF addition.

Table 4.1 Analysis of FT-IR spectra of the original MEH-PPV and modified MEH-PPV. The polymer solutions were mixed with 10 vol.-% PF and left to age for 75 days. Original concentrations of MEH-PPV are shown in the table

MEH-PPV		Assignment
Original	Modified	
-	* 682	CH bending vibrations in CH deformation
-	* 777	CH out-of-plane bending vibrations in -CH=CH-(cis) group
+ 875	-	CH out-of-plane bending vibrations in -C=CH$_2$ group
+ 966	958	CH out-of-plane bending vibrations in -CH=CH-(trans) group
+ 1040	1020	aryl alkyl ether (C-O-C) symmetric stretching vibrations in acetates group
+ 1190	1190	aryl alkyl ether (C-O-C) stretching vibrations in formates group
+ 1200	1200	ring stretching vibrations and CH deformation
+ 1250	1270	aryl alkyl ether (C-O-C) asymmetric stretching vibrations in benzoates group
+ 1350	-	CH bending vibrations in -CH$_3$ deformation
+ 1410	1410	CH bending vibrations in -CH$_2$ deformation
+ 1460	1440	asymmetric CH bending vibrations in -CH$_3$ group
1500	* 1490	C=C stretching vibrations in conjugated
-	* 1630	C=C stretching vibrations in non-conjugated
2860	2860	symmetric CH stretching vibrations in -CH$_2$ group
2930	2930	asymmetric CH stretching vibrations in -CH$_2$ group
2950	2950	asymmetric CH stretching vibrations in -CH$_3$ group
3060	* 3040	CH stretching vibrations in =C-H, =CH$_2$ group and CH group
-	* 3130	NH stretching vibrations in H bonded NH group
-	* 3420	OH stretching vibrations of intramolecular H bonds

* = The intensity of the peak was greatly increased after PF addition.

+ = The intensity of the peak was greatly decreased after PF addition.

Figure 4.10 illustrates FT-IR spectra of the original MEH-PPV along with that of the modified one. The modified MEH-PPV was obtained by reacting with 10 vol.-% PF for 75 days. We note that the use of 0.01, 0.005 and 0.001% (w/v) of the original MEH-PPV solutions leads to the same FT-IR pattern of the dried samples. This indicates that the solvent and PF are completely removed from the

samples, which is confirmed by the absence of the FT-IR spectrum of the pure PF (not shown). Table 4.1 summarizes some absorption peaks corresponding to different vibrational modes of the polymeric segments. It is apparent that the absorbance of the peaks at 1040, 1190 and 1250 cm^{-1} of the original MEH-PPV is greatly reduced in the modified polymer. Since these peaks are specific to the vibrations of aryl–alkyl ether linkage (C-O-C) of the MEH side groups, this indicates the reduction in the number of MEH side groups in the modified MEH-PPV. In addition, the concentration of tetrahedral defects along the polymeric main chain appears to increase significantly. This is indicated by the detection of new intense peak at 1630 cm^{-1} in the modified MEH-PPV, which is specific to the C=C stretching vibration of the non-conjugated chains. In other words, a number of the C=C bonds is converted to single bonds, which interrupt the conjugation along the conjugated backbone. The detection of a broad peak at 3420 cm^{-1} also indicates the presence of hydroxyl groups in the modified MEH-PPV. These results suggest that the reaction between MEH-PPV and PF results in the reduced number of MEH side groups and the increased number of non-conjugated segments, which are responsible for the observed decrease in the conjugation lengths of the modified polymer.

4.5 Conclusions

We have demonstrated a versatile method for tuning the optical properties of one of the most investigated conjugated polymers, MEH-PPV. This is accomplished by the reaction of the polymer with pyridinium formate (PF), a volatile organic salt. The absorption and the emission spectra (i.e., colors) of the modified MEH-PPV can be controlled by the variations in the concentration of PF and the reaction time. This method results in the displacement of the λ_{max} of the absorption spectra and the emission spectra by 60 nm and 15 nm, respectively. The size distribution of chromophores in the main chain is also affected significantly. The modified MEH-PPV chains contain a larger number of shorter chromophores. Structural analysis by using NMR and FT-IR spectroscopy indicates that the variation in the optical properties arises from the breaking of some double bonds along the conjugated chains and the removal of MEH side groups. The extent of

these structural changes dictates the optical properties of the modified MEH-PPV. The results obtained in this work signify the ability to systematically tuning the optical properties of MEH-PPV, which can be utilized for a wide range of applications such as OLED and solar cells. Our method is a one step process which is much simpler compared to the common copolymerization approach. It also requires relatively cheap chemicals and takes a simple procedure for purification.

4.6 Acknowledgments

4.7 References

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