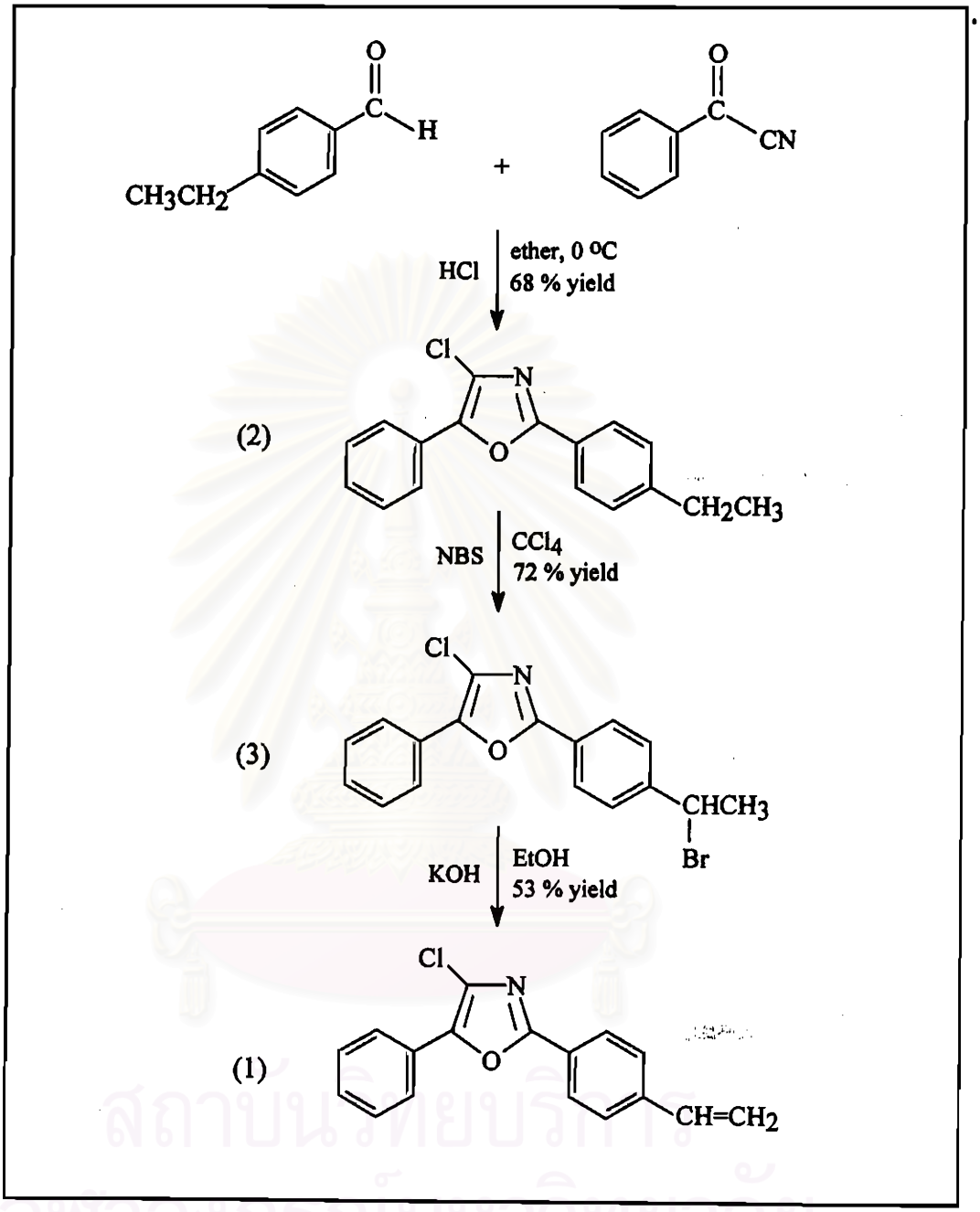
Chapter IV

Results and Discussions

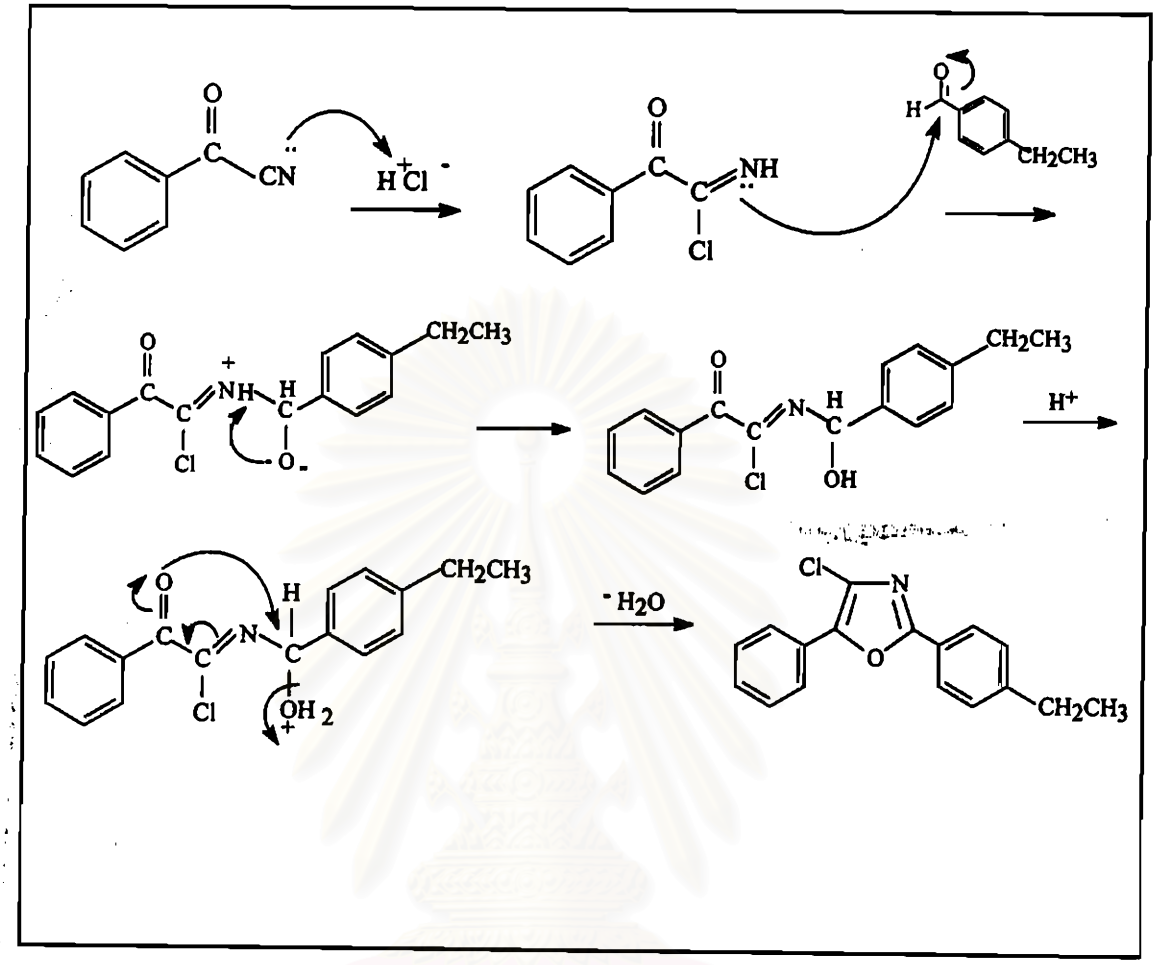
Part I : Synthesis of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole (1)

The 4-Cl-(vinyl)-PPO (1) required was prepared by a 3-step reaction sequence (scheme 4.1). The synthetic route started from the preparation of 4-Cl-(Et)-PPO (2) by using the Ternai method [25], which is the most efficient method due to the high yield and lack of by-products. Since the presence of a chloro-substituent at C-4 of the oxazole ring has only negligible effect on the fluorescence and scintillation efficiency [2,3], it was not removed.

4-Cl-(Et)-PPO has been obtained from the cyclization of benzoyl cyanide reacting with *p*-ethylbenzaldehyde and saturated with hydrogen chloride. The proposed mechanism of this reaction is shown in scheme 4.2. The crude product was recrytallized from methanol, colorless needle-like crystals, mp 68-70 °C: 68 % yield.



Scheme 4.1



Scheme 4.2

The IR spectrum of 4-Cl-(Et)-PPO (Figure A1) is compared with the spectra of PPO and 4-Cl-PPO (Figure A29 and A30). There are the new peaks in both of the chloro compound at 1280 and 1214 cm^{-1} while 4-Cl-(Et)-PPO exhibits absorption peaks at 1277 and 1217 cm^{-1}. These peaks appear at about double the frequency normally assigned to C-Cl stretching. They are thought to be due to C-Cl bending. All these above oxazole derivatives exhibit an absorption peak at 1580 cm^{-1} which was assigned to the vibrations arising from oxazole ring system [41]. Comparison of 4-Cl-(Et)-PPO with PPO and 4-Cl-PPO is shown in Table 4.1.

Table 4.1 : Interpretation of IR spectra of PPO, 4-Cl-PPO, 4-Cl-(Et)-PPO

Wave number, cm^{-1}			Assignment
PPO	4-Cl-PPO	4-Cl-(Et)-PPO	
3057	3047	3018	arom. C-H stretching
-	-	2962	aliphatic C-H stetching
1593	1598	1580	C=C
1485	1480	1490	C-N
-	1280 1214	1277 1217	C-Cl bending
691	681	685	arom.C-H deformation

The ^{1}H NMR spectrum (Figure A2) of 4-Cl-(Et)-PPO in chloroform-*d* exhibits the characteristic ethyl triplet at 1.24-1.29 (J=7.5 Hz) ppm coupled with a quartet at 2.75-2.63 (J=7.5 Hz) ppm due to the $-CH_3-$ and $-CH_2-$ of the ethyl group. The chemical shifts of aromatic protons appear at 8.00-7.90 (5H) and 7.50-7.27 (4H).

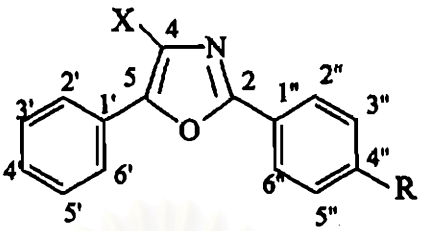
The assignment of ^{13}C NMR spectrum of 4-Cl-(Et)-PPO (Figure A3) can be achieved by comparing the spectra of PPO and 4-Cl-PPO (Table 4.2). Firstly, the carbons of the oxazole ring in PPO can be assigned by using the phenyl group substituent effect on the C-2 and C-5 of oxazole itself [42]. The calculated chemical shift positions of C-2, C-4 and C-5 are 163.00, 131.40 and 151.00 ppm, respectively. These are consistent with the chemical shifts found in PPO, therefore the peaks at 161.06, 130.20 and 151.19 in PPO are assigned for C-2, C-4 and C-5, respectively. The resonances of the phenyl carbons in PPO in the range of 124.84-123.43 ppm are similarly assigned by using substituent effect rules. For 4-Cl-PPO, the resonance of C-4 can be calculated by adding the -Cl group effect to C-4 of PPO. Since the -Cl is an electron withdrawing group, it causes a downfield shift of the C-4 in 4-Cl-PPO to 143.92 ppm. For 4-Cl-(Et)-PPO, the C-4 appear at 143.48 ppm and the resonances of the ethyl carbons appear at 28.86 ($-CH_2-$) and 15.54 ($-CH_3$) ppm.

The bromination of 4-Cl-(Et)-PPO was carried out by NBS/CCl_4 (initiated by benzoyl peroxide) to yield 4-Cl-(BrEt)-PPO (3) as a white crystalline product in 72 % yield. A free radical mechanism is involved and hence the bromination took place almost exclusively at the secondary, more stable, carbon. The FTIR spectrum of 4-Cl-(BrEt)-PPO (Figure A6) exhibited an absorption band at 593 cm^{-1} (C-Br); this band is also present in bromoethylbenzene and is absent in ethylbenzene. ^{1}H NMR spectrum (Figure A7) shows the -CHBr- peak at 5.23 (q, J = 6.9 Hz) and a $-CH_3$

peak at 2.07 (d, J = 6.9 Hz) ppm. The ^{13}C NMR spectrum of 4-Cl-(BrEt)-PPO exhibit signals of -CH_3 and -CHBr- at 26.44 and 48.29 ppm. The aromatic signals were at 128.84-125.01 ppm while the oxazole carbons showed peaks at 158.02 (C-2), 149.95 (C-5) and 140.41 (C-4) ppm.

The vinyl-substitued PPO, [4-Cl-(vinyl)-PPO (1)], was prepared by nucleophilic attack on the bromoethyl compound by excess potassium hydroxide in ethanol. Nitrogen atmosphere and inhibitor were required for this step since the vinyl group could be easily polymerized. Comparison of the IR spectra of compounds 4-Cl-(BrEt)-PPO and 4-Cl-(vinyl)-PPO in Figure A6 and A11 reveals the absence of the peak at 593 cm^{-1} (thought to be due to C-Br stretching). The ^1H NMR (Figure A12) of 4-Cl-(vinyl)-PPO showed a quartet centered on 6.74 for the -CH= and 5.85 and 5.36 for the =CH_2 trans- and cis- protons, respectively (The shift and J values of this ABX spectrum were not calculated). The ^{13}C NMR (Figure A13) of 4-Cl-2-(4′-vinyl)-PPO confirmed the identity of the product. Since the C-1 of PS is at 138.2 ppm. The resonance of C-1″ in 4-Cl-(vinyl)-PPO appears downfield at chemical shift 140.05 ppm. The ^{13}C assignments of PPO, 4-Cl-PPO, 4-Cl-(Et)-PPO and 4-Cl-(vinyl)-PPO are shown in Table 4.2.

Table 4.2 : Assignments for the ^{13}C-NMR spectra of PPO, 4-Cl-PPO, 4-Cl-(Et)-PPO and 4-Cl-(vinyl)-PPO.



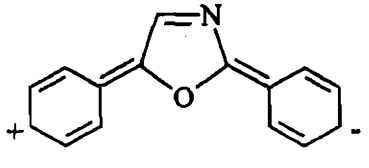
Chemical Shift (ppm)				Assignments
X=R=H	X=Cl, R=H	X=Cl, R=Et	X=Cl, R= Vinyl	
161.06	159.13	159.18	158.81	2
151.19	147.55	147.65	149.50	5
130.20	143.92	143.48	143.85	4
124.84	130.98	128.76	140.05	4''
128.27	128.91	128.49	128.83	2'',6''
128.33	128.91	128.39	128.66	3'',5''
128.00	128.84	126.95	128.44	1''
127.47	128.68	126.38	126.68	2',6'
126.22	126.92	126.22	126.55	1'
124.13	126.36	124.87	125.54	3',5'
123.43	125.02	123.87	125.00	4'
-	-	26.86 15.54	135.97 115.85	1''' 2'''

The λ_{max} and ε_{max} of PPO, 4-Cl-PPO and three of oxazole synthesized in this work are shown in Table 4.3.

Table 4.3 : UV absorption spectral data of PPO, 4-Cl-PPO, 4-Cl-(Et)-PPO, 4-Cl-(BrEt)-PPO and 4-Cl-(vinyl)-PPO in dichloromethane

Oxazole	λ_{max}	log ε_{max}
PPO	305	4.34
4-Cl-PPO	308	4.40
4-Cl-(Et)-PPO	310	4.47
	318	4.46
	326	4.43
4-Cl-(BrEt)-PPO	319	4.43
4-Cl-(vinyl)-PPO	325	4.50
	260	4.10

All three of these synthesized oxazoles have λ_{max} near that of the parent compound, PPO, which has a λ_{max} at 305 nm. However, Brown and Ghosh [43] showed that PPO in methanol exhibits two main peaks, of which the high intensity one at 314 nm (log ε = 4.34) and low one at 244 nm (log ε = 4.08), are due to the resonance contribution by the quinonoid form below. The polarity of methanol is higher than dichloromethane hence it will enhance the contribution of this polarized form.



The λ_{max} of 4-Cl-(Et)-PPO appears at 310 nm (Figure A4). It is compared with the spectra of PPO and 4-Cl-PPO in Figures A31-32. The absorption between 250-280 is flat in 4-Cl-PPO and in 4-Cl-(Et)-PPO, therefore there might be a peak at this wavelength. There are also an absorption shoulder at about 242 nm in 4-Cl-PPO and peak at 244 nm in 4-Cl-(Et)-PPO which occurs in the same place in styrene as a primary absorption band [44]. These absorption trend is also due to the conjugation of quinonoid form.

The 4-Cl-(BrEt)-PPO has λ_{max} at 320 nm which is longer wavelength than 4-Cl-(Et)-PPO since halogens are auxochromes. Changing from the ethyl to a vinyl group causes the absorption band to shift towards longer wavelengths. The observation that 4-Cl-(vinyl)-PPO absorbs at λ_{max} = 326 nm which is higher than 4-Cl-(Et)-PPO, can be attributed to the extended conjugation cf. ethylbenzene (λ_{max} = 260 nm) and styrene (λ_{max} = 282 nm).

Fluorescence emission spectra of these 4-Cl-PPO derivatives shows band at λ_{max} 312, 375 and 396 nm for the ethyl, bromoethyl and vinyl substitued 4-Cl-PPO, respectively. The bathochromic shifts are seen when changing the ethyl to a vinyl group as a result of extended conjugation with the double bond. The absorption/fluorescence evidently is due to π π^* transition.

Part II : Synthesis of polymers

Poly[4-Cl-PPO-co-styrene] with various mol ratios of the monomers were prepared by bulk polymerization with a free radical initiator. The copolymers were obtained as pale yellow viscous solids, soluble in aromatic and chlorinated solvents and insoluble in cyclohexane, methanol and water. They were characterized by UV absorption and fluorescence emission spectroscopy.

The extent of the incorporation of the oxazole moiety into the poly[4-Cl-PPO-co-styrene] were determined by nitrogen analysis (Figure 4.1). The relative extent of 4-Cl-PPO incorporation decreases with increased amounts of the added 4-Cl-PPO monomer.

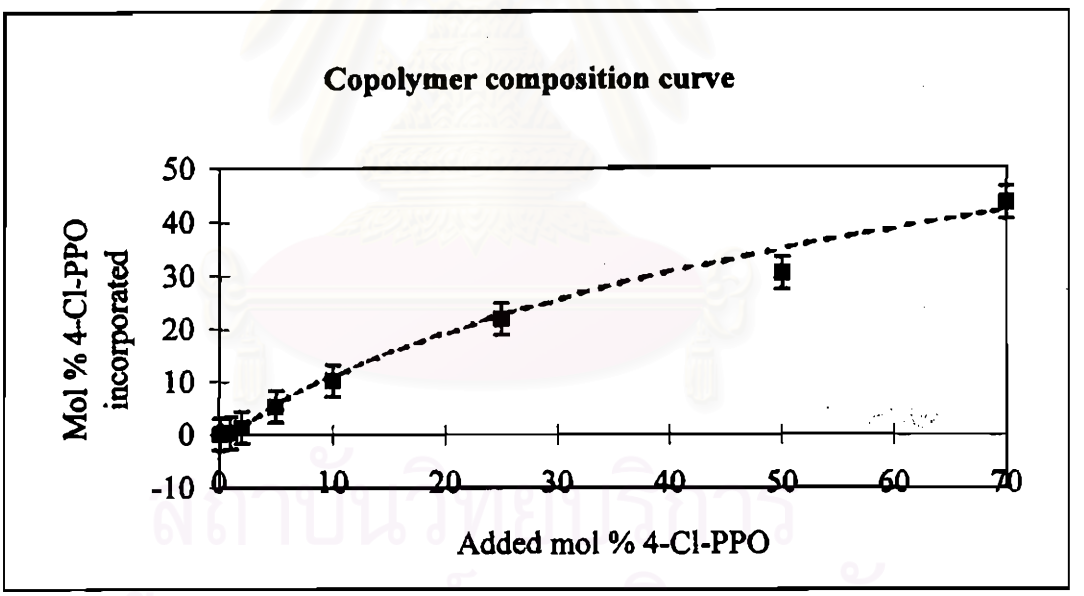


Figure 4.1 : Incorporation of 4-Cl-PPO poly[4-Cl-PPO-co-styrene]

Part III : UV and fluorescence analysis of Poly[4-chloro-2-(4'-vinyl phenyl)-5-phenyloxazole-co-styrene]

1. Poly[4-Cl-PPO-co-styrene] in dichloromethane

The UV absorption and fluorescence emission properties of poly[4-Cl-PPO-co-styrene] in dilute solution were studied. The choice of suitable solvent is limited by the solubility of the copolymer. Dichloromethane was found to be satisfactory with its UV cutoff at 230 nm. It is assumed that the absorption and the fluorescence behaviour of the copolymers is not significantly influenced by the terminal groups due to the initiator. Although these groups might quench fluorescence, they were present in very low concentration. The dilute poly[4-Cl-PPO-co-styrene] solutions of 5 mg/100 mL and 1 mg/100 mL CH_2Cl_2 were analyzed. Typical UV and fluorescence emission spectra of the copolymer in dichloromethane are shown in Figures A19 - A25.

In the UV absorption spectra of the poly[4-Cl-PPO-co-styrene] 5 mg/ 100 mL CH_2Cl_2 (Figure A19) the prominent band at λ_{max} of 312 nm is due to the 4-Cl-PPO, which appears at λ_{max} = 308 nm in 4-Cl-PPO (Figure A32) and is absent in the spectrum of PS (Figure A17). The absorption at 260 nm is present in both monomers and hence can be attributed to the phenyl chromophore although the intensity of this peak in the copolymer is much reduced. 4-Cl-PPO moiety in the copolymer absorbs at virtually the same wavelength (λ_{max} = 312 nm) compared to 4-Cl-(ethyl)-PPO in dichloromethane (λ_{max} = 310 nm), indicating that copolymerization has in fact taken place.

When excited at the wavelength of 260 nm, the fluorescence spectra of poly[4-Cl-PPO-co-styrene] with mol % of 4-Cl-PPO 0.05-9.98 % exhibit two main bands, at 307 and 375 nm. The phenyl chromophore from polystyrene emits at 307 nm (Figure A17). The 4-Cl-PPO chromophore in the copolymer emits at 375 nm while 4-Cl-(vinyl)-PPO emits at 395 nm. At high mol % of 4-Cl-PPO (21.9-43.5 %) the peak at 307 nm disappears and the intensity at 375 nm is lower due to self quenching, hence poly[4-Cl-PPO-co-styrene] solutions of 1 mg/100 mL in dichloromethane were analyzed.

In order to establish the extent of the interaction between the aromatic rings of the two monomers the concentration dependence of the UV absorbance of the individual monomers have been compared. The absorption spectra of polystyrene and its model, ethylbenzene, are very similar, indicating the absence of any strong ground-state between the chromophore [29]. Since both ethylbenzene and 4-Cl-(Et)-PPO absorb at 260 nm, it is reasonable to assume that if no interaction takes place between the two chromophores, the absorbances at 260 nm are additive. The ε_{260} of ethylbenzene is 263 $Lcm^{-1}mol^{-1}$ and ε_{260} of 4-Cl-(Et)-PPO is 9650 Lcm^{-1} mol^{-1}. Since concentrations of the monomers are known, hence the expected absorbance at 260 nm can be calculated, assuming no interactions.

Comparison between the calculated and measured A_{260} (Figure A22) is shown in Figure 4.2. The graph indicates that both absorbances are linear. Above 10 mol % of 4-Cl-PPO the calculated absorbance is much higher than the experimental values. Therefore there are some quenching occur due to interaction between the two chromophores above 10 mol % of 4-Cl-PPO. According to the graph, when the mol % of 4-Cl-PPO increases, the interaction also increases as expected.

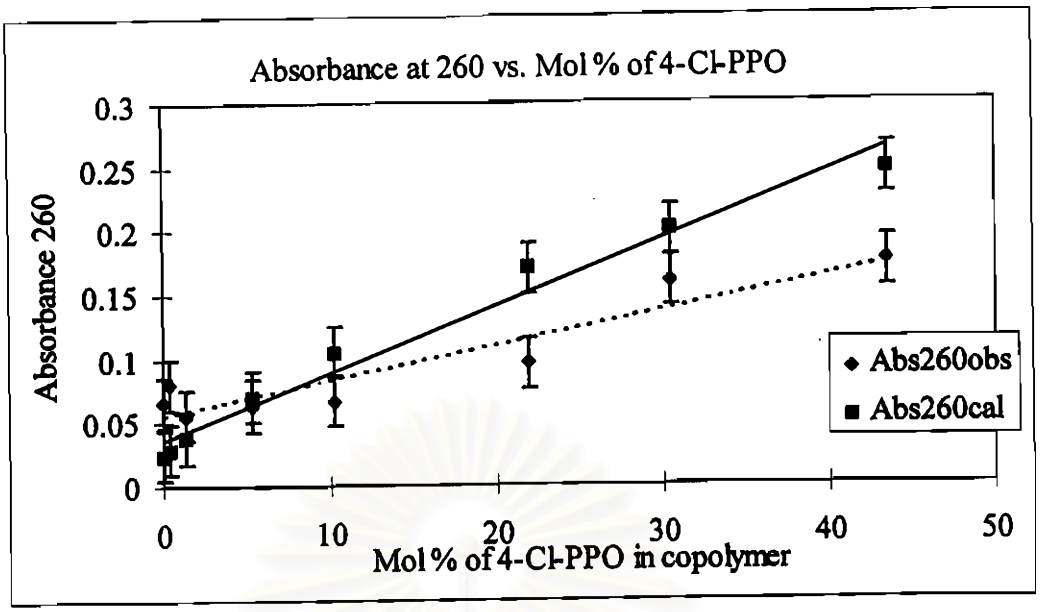


Figure 4.2 : Calculated and measured absorbance at 260 nm vs. mol % of 4-Cl-PPO in poly[4-Cl-PPO-co-styrene]

The fluorescence of poly[4-Cl-PPO-co-styrene] with excitation wavelength at 260 nm in air and deoxygenated solution (Figures A23 and A24) exhibit the same shape of fluorescence spectra. Since oxygen in air has the ability to quench fluorescence, the deoxygenated solutions show higher intensity at all mol % of the copolymer. The intensities at 375, 390 and 420 are plotted vs. the mol % of 4-Cl-PPO in the copolymer in Figure 4.3. A decrease in the intensity at 375 nm relative to the intensity at 390 and 420 nm is observed when the mol % of 4-Cl-PPO increased (Table 4.4). This indicates that quenching is significant at higher concentrations of the fluorescence agent.

Figure 4.3 : Intensities at 375, 390 and 420 nm vs. mol % of 4-Cl-PPO in poly[4-Cl-PPO-co-styrene]

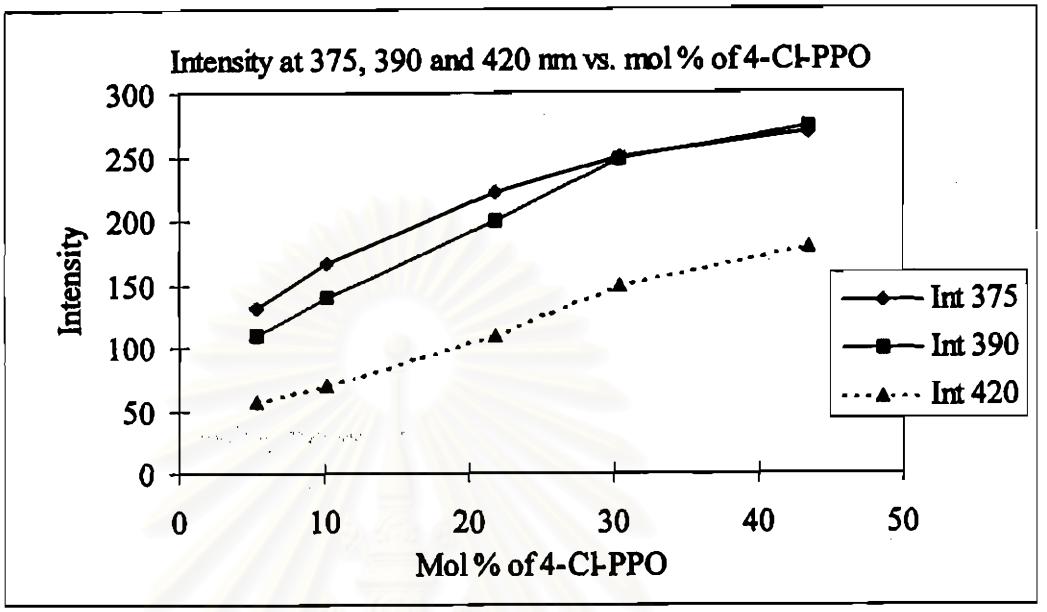


Table 4.4 : Intensity at 375/390 and 375/420 nm ratios for poly[4-Cl-PPO-co-styrene] 1 mg/100 mL CH_2Cl_2 solution (air), excitation at 260 nm

Mol % of 4-Cl-PPO in the copolymer	Int_{375}/Int_{390}	Int_{375}/Int_{420}
4.48	1.17	2.29
9.98	1.15	2.37
21.9	1.11	2.02
30.5	1.00	1.70
43.5	0.98	1.50

Comparisons were made between the % absorption and the % emission of the 4-Cl-PPO moiety in poly[4-Cl-PPO-co-styrene] solutions with the same mol ratios. Figure 4.4 shows % absorption of the 4-Cl-PPO moiety at wavelength 260 nm from the absorption spectra and % emission of this chromophore from the fluorescence emission spectra which was excited at 260 nm vs. mol % of 4-Cl-PPO in poly[4-Cl-PPO-co-styrene].

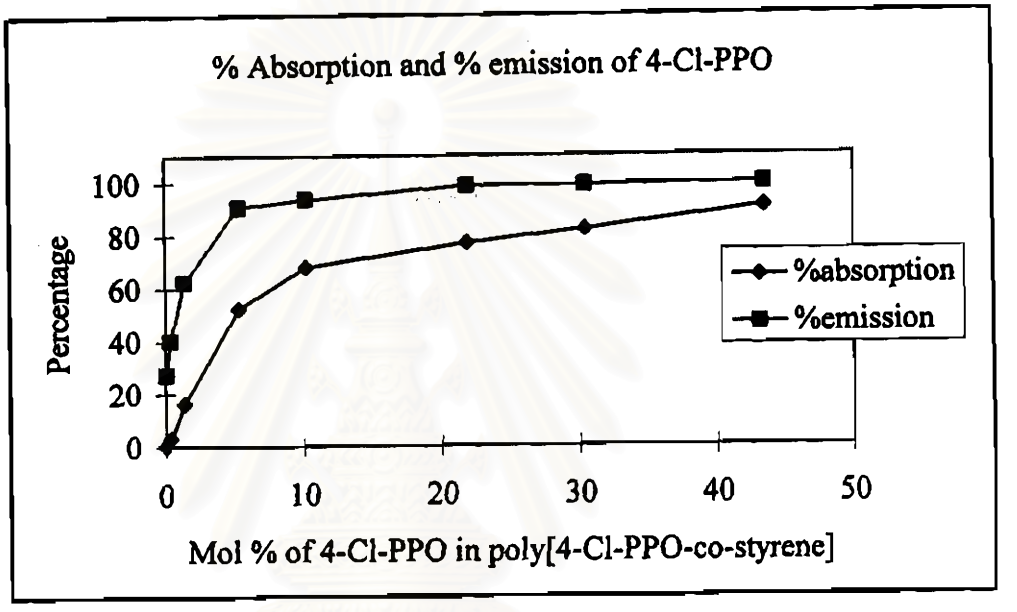


Figure 4.4 : % absorption$_{4\text{-Cl-PPO}}$ at 260 nm and % emission$_{4\text{-Cl-PPO}}$ of poly[4-Cl-PPO-co-styrene], excitation at 260 nm in CH_2Cl_2 (1mg/100mL)

Figure 4.4 shows that the % emission is higher than the % absorption of 4-Cl-PPO in all mol ratios of poly[4-Cl-PPO-co-styrene]. This indicates that energy transfer could occur in dilute solution of copolymer in dichloromethane. Since the S_1 state of the polystyrene chromophore has an energy of 93.7 kcal/mol while the S_1 state of the 4-Cl-PPO is at 76.2 kcal/mol [45], it is reasonable to assume that the excited singlet polystyrene chromophore has transferred its excitation energy to the 4-Cl-PPO moiety and the fluorescence emission is mainly due to the excited 4-Cl-PPO molecule (Figure 4.5).

For this reason it is assumed that poly[4-Cl-PPO-co-styrene] at low concentration shows intramolecular interaction and the energy transfer mechanism may be by dipole-dipole interaction through the polystyrene coils, followed by eventual transfer to a 4-Cl-PPO group. At higher concentrations the 4-Cl-PPO suppresses excimer formation as seen by a decrease in the Intensity 375/Intensity 390 ratios. The fluorescence spectrum (Figure A25) of the poly[4-Cl-PPO-co-styrene] solution excited at 320 nm shows a higher intensity when it is excited at 260 nm. This reflects the higher ε value at the wavelength of 320 nm.

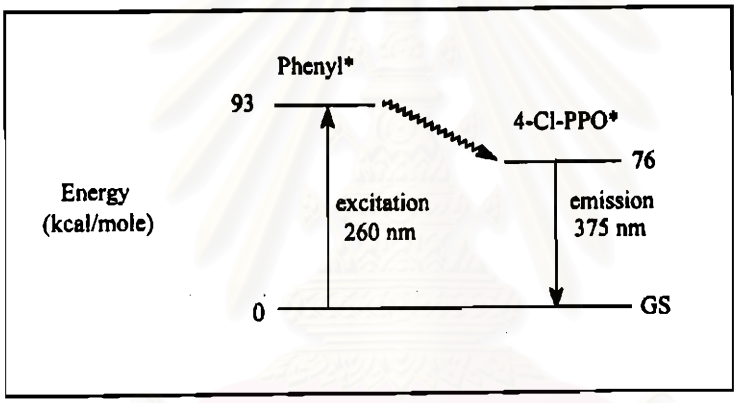


Figure 4.5 : Energy transfer process of poly[4-Cl-PPO-co-styrene] in CH_2Cl_2 solution

2. Poly[4-Cl-PPO-co-styrene] film

In this work, the emission spectra of all poly[4-Cl-PPO-co-styrene] films were measured at room temperature with an excitation wavelength of 260 nm. At this wavelength the phenyl chromophore from both monomers is directly excited. It might be thought that changing the mol ratio of the monomers in the copolymer is equivalent to changing the solute in a solvent. However, this is not the case here. It should also be noted that the configuration of the polymer coils that make up the film may be dependent on the actual casting conditions (temp, solvent, etc.).

Poly[4-Cl-PPO-co-styrene] with low concentrations of 4-Cl-PPO units (0.05-1.37%)

Films of poly[4-Cl-PPO-co-styrene] containing small proportions of 4-Cl-PPO shows fluorescence spectra which are similar to those of the solutions. The emission spectra of 0.05 % 4-Cl-PPO chromophore (Figure A26) , it exhibits a structured band with λ_{max} at 307 nm due to polystyrene and λmax at about 395 nm due to the 4-Cl-PPO chromophore. The fluorescence spectra shows that 4-Cl-PPO chromophore emits light 70 % and only 30 % of light is emitted by polystyrene chromophore. The fluorescence emission is mainly due to the 4-Cl-PPO chromophore instead of the polystyrene chromophore. So it is possible to say that energy transfer processes have taken place in the copolymer film.

The emission spectra of 0.38 and 1.37 mol % of 4-Cl-PPO in the poly[4-Cl-PPO-co-styrene] are shown in Figure A26. The spectra shows a decrease in the intensity of the fluorescence from polystyrene and an increase in the intensity of the fluorescence from the 4-Cl-PPO chromophore which emit light 62 and 100 % for 0.38 and 1.37 mol% of 4-Cl-PPO in the copolymer, respectively. However, the poly[4-Cl-PPO-co-styrene] films containing larger amounts of 4-Cl-PPO exhibit different spectra.

Poly[4-Cl-PPO-co-styrene] with concentration of 4-Cl-PPO units (4.88-43.48 %)

Figure A27 shows the emission spectrum of poly[4-Cl-PPO-co-styrene] film with 4.88 mol% of 4-Cl-PPO units. The spectrum exhibits a broad and unstructured band with a λmax at 395 nm. Above 9.98% of 4-Cl-PPO content, the fluorescence spectra of the copolymer films contain two main bands:

- a simple mirror image of the absorption band at 395 nm
- a broad unstructured band appears at 460 nm

Since this emission band appears at longer wavelength than the emission of 4-Cl-PPO, it is attributed to an excimer state (a dimeric species formed between an excited 4-Cl-PPO and another one in ground state) which occurs in the copolymer film. The band at 460 nm indicates that the excimer has an energy of 62 kcal/mole above the ground state.

An energy level diagram which illustrates excimer formation is shown below.

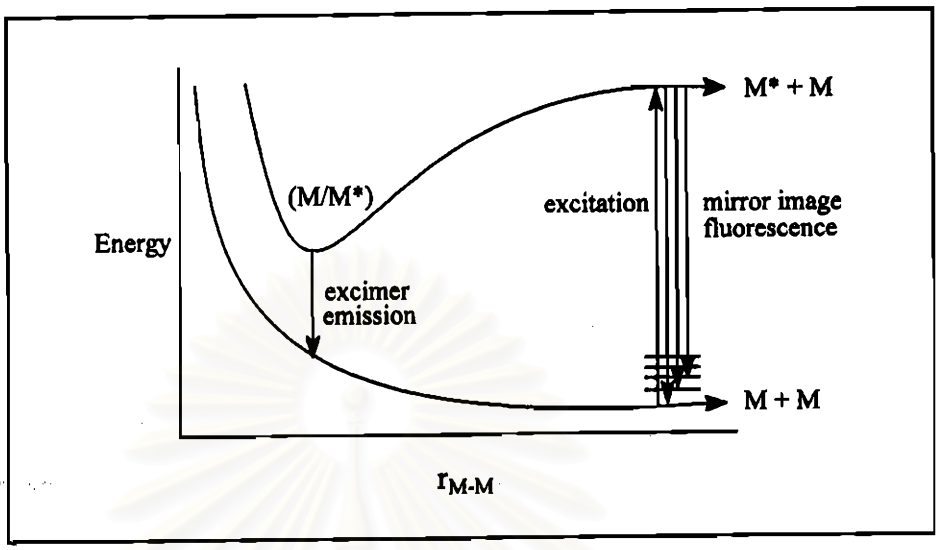


Figure 4.6 : Excimer formation in in poly[4-Cl-PPO-co-styrene] films

Generally, excimer formation is dependent on the distance or internuclear separation between the two molecules. If there is no interaction between M* and M, the fluorescence spectra will have a structured band from S_1 to S_0. When excimer interaction occurs, smaller energy gap (ΔE) results in emission at a longer wavelength and the excimer returns to the unstable ground state which has an unquantized vibration state and therefore shows no structure in the fluorescence emission. It should be noted that the absorbance of the excimer does not obey the simple Lambert-Beer Law, since formation and the dissociation of the excimer depends on the concentrations [29].

The emission spectra of 21.48, 30.45 and 43.48 mol % of 4-Cl-PPO in poly[4-Cl-PPO-co-styrene] films are shown in figure A28, The spectra exhibit the fluorescence band mainly due to excimer emission and the mirror image fluorescence decreases when the amount of 4-Cl-PPO in copolymer film increases. This is possibly because in the copolymer film the intensity of excimer emission is proportional to the amount of 4-Cl-PPO and the interaction is mainly due to the way these molecules are aligned in the film.

The intensities of the normal emission, I_M and the excimer emission, I_D, were measured at 395 and 460 nm, respectively. Since I_D/I_M ratios provide a convenient, albeit relative, experimental measure of the degree of separation between a chromophore, the plot between the intensity ratio of excimer and mirror image fluorescence versus mol % of 4-Cl-PPO in the copolymer is shown in Figure 4.7.

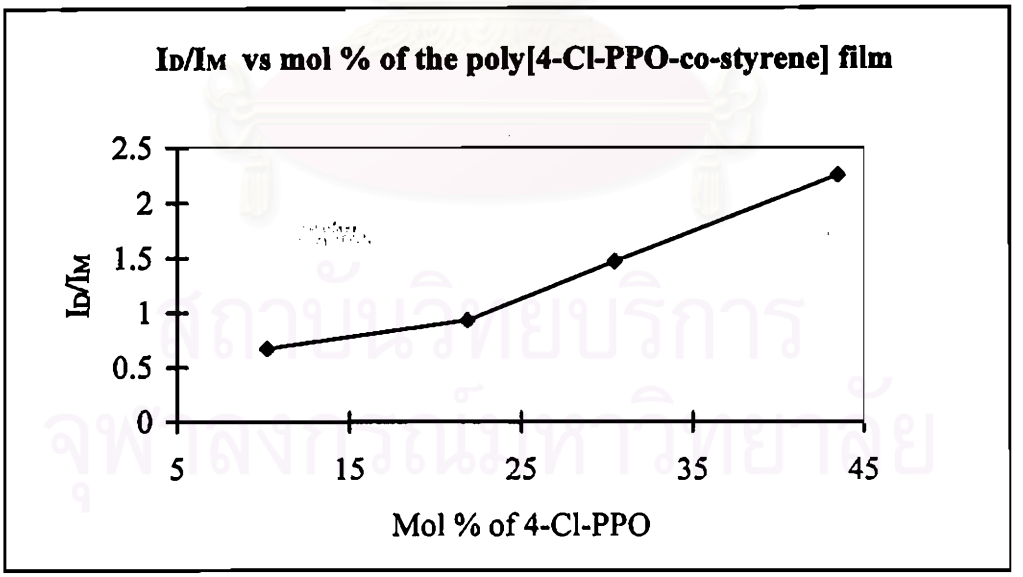
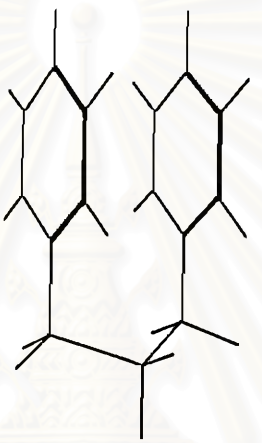


Figure 4.7 : Excimer/normal fluorescence intensity ratios (I_D/I_M) for copolymer films vs. mol % of 4-Cl-PPO in poly[4-Cl-PPO-co-styrene], excitation at 260 nm

The graph indicates that I_D/I_M increase as a function of mol % of 4-Cl-PPO in the poly[4-Cl-PPO-co-styrene] films. This is consistent with previous observations on other types of copolymer [28]. Above 21.89 % of 4-Cl-PPO content, fluorescence emission is mainly due to excimer formation. Generally, intramolecular transfer would be expected not to depend on the polymer concentration i.e., the excimer fluorescence from dilute polymer solution occurs due to interaction between adjacent chromophores of polymer coils, whereas an intermolecular process would be relatively dependent of concentration [27]. Since interchain chain coiling can produce geometry favorable to excimer formation between non-adjacent chromophores, the increase in I_D/I_M for the films could be attributed to interchain excimer formation. However, both intra- and interchain interaction are possible in these copolymer films.

Excimers are observed in all of these aromatic polymers under a variety of conditions and, particularly in bulk polymers, excimer emission will predominate over the normal emission from mirror image fluorescence [28]. It is now generally accepted that in certain solid aromatic vinyl polymers excimer emission occurs after an initial excitation of an aromatic chromophore, followed by intramolecular singlet energy transfer, either along the polymer chain, or intermolecular transfer between chromophores in different chains in the bulk phase until the excitation is competitively trapped at a chain conformation which is geometrically suitable for excimer formation. In polystyrene, the interaction between the phenyl rings of polymer is very efficient. It is now established that the excimer in the polystyrene are formed between neighboring phenyl groups [33, 34].

Emission and absorption of solution of PS, have many of the features consistent with those of the 1,3-diphenylpropane which closely resemble the structure of the two neighboring side groups of the polymer. The excimer should have a gauche-gauche conformation. The studies of molecular models of this arrangement suggest that the spacing of the rings in the excimer should be 2.54 Å [27]. In fact, the excimer formation rarely observe in this compound since the conformation is highly repulsive and require high energy formation (not stable).



1,3-diphenylpropane

The structures of poly[4-Cl-PPO-co-styrene] in solutions and solid state are shown in Figure 4.8. The results from dilute copolymer solutions exhibit different spectra from those of films. When comparing the fluorescence spectra of the copolymer films (Figures A26-A28) to the spectra of copolymer solution (Figure A23), the 4-Cl-PPO concentration in films is very high and usually excimer is predominants while 4-Cl-PPO in the solution suppressed excimer formation at high mol % of 4-Cl-PPO moiety.

It is reasonable to assume that in copolymer film, the polymer chains are close packed (Figure 4.8 a) and strong interactions may occur, especially if the groups are favorably spaced and oriented relative to each other. Therefore, intermolecular interaction is likely to occur. In poly[4-Cl-PPO-co-styrene], the excimer might take place between phenyl chromophore of polystyrene and another phenyl chromophore of 4-Cl-PPO group. It can suggest that the polymer chain in these copolymer films arrange like layer (Figure 4.8 c). However, the random coil molecule of copolymer solution (Figure 4.8 b), on the other hand, behave more like model compounds and only weak interactions between the chromophores can be identified. The chance to form sandwich structures is less as the polymer solution is diluted and the intramolecular interactions are mainly occur.

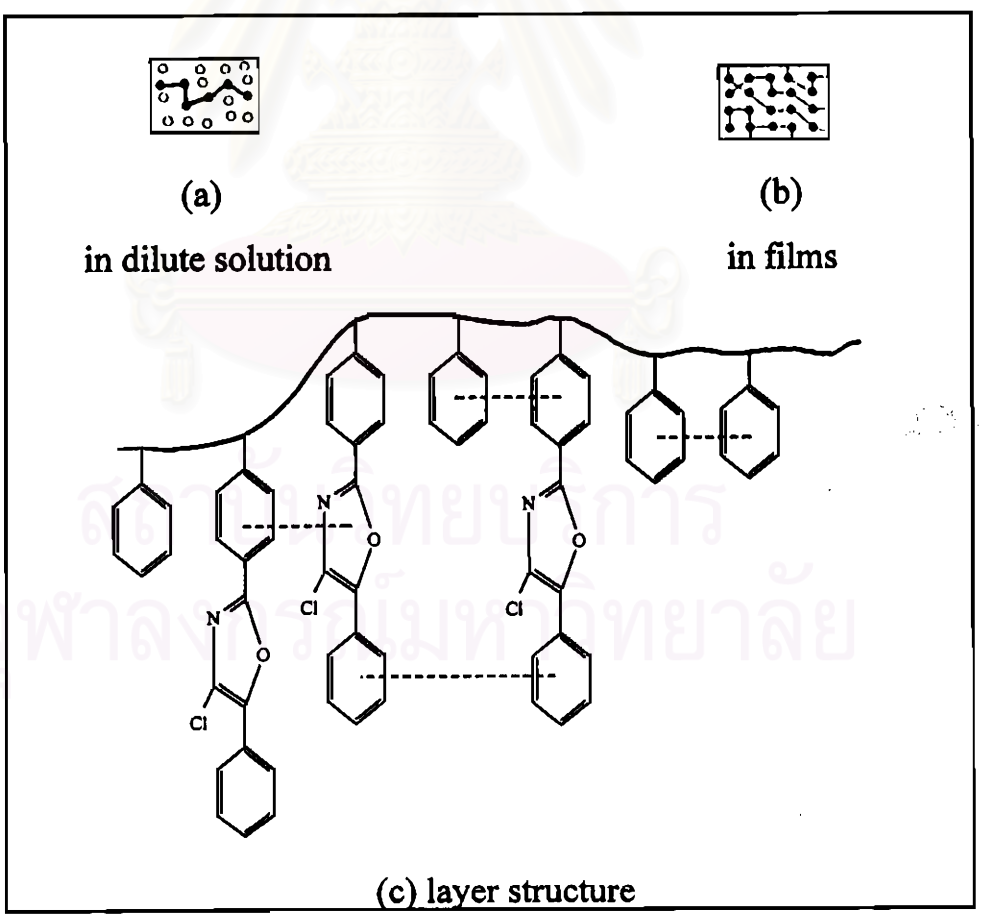
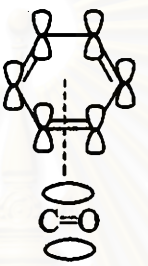


Figure 4.8 : The structure of the poly[4-Cl-PPO-co-styrene]

Poly[4-Cl-PPO-co-MMA] film (Figure A33) shows a peak at 520 nm when excited at 260 nm. Eventhough this sharp peak appears at longer emission wavelength than 4-Cl-PPO moiety but it is not due to the formation of the excimer as observe in poly[4-Cl-PPO-co-styrene]. It is reasonable to assume that this 520 nm peak is due to the π-π interaction between carbonyl group of MMA with the phenyl ring of 4-Cl-PPO. Therefore, it indicates that this peak can be attribute to the *exciplex* (excited complex).



Exciplex formation in poly[4-Cl-PPO-co-MMA]

<u>Part IV</u> :Fluorescence quantum yields measurement of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-styrene copolymer

The overall efficiency of the fluorescence process ($S_1 \rightarrow S_0$) of the molecule is usually described by the fluorescence quantum yield, ϕ_{fl} which is defined as:

$$\phi_{fl} = \frac{\text{no. of molecules undergoing a fluorescence process}}{\text{no. of photons absorbed by the system}}$$

$$\frac{\phi_{sample}}{\phi_{p\text{-}xylene}} = \frac{\text{total are under emission curve of sample}}{\text{total area under emission curve of p-xylene}}$$

In this work, the total areas under fluorescence emission curve of poly[4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-styrene] were measured (Table 3.4 and 3.5). *p*-Xylene in dichloromethane was used as a standard with the $\phi_{p\text{-xylene}}$ value is 0.33 [40]. Since the total area of *p*-xylene emission curve is equal to 30870.36 (arbitrary unit), then the apparent ϕ_{fl} of the copolymer can be calculated by comparing the area under emission curve of the copolymer with the area of the standard. Table 4.5 shows the apparent fluorescence quantum yields of the copolymers in air and deoxygenated solutions.

Table 4.5 : Apparent fluorescence quantum yield of poly[4-Cl-PPO-co-styrene] in air and degassed solution

Mol % 4-Cl-PPO in the copolymer	apparent ϕ_{fl} in air-saturated solution	apparent ϕ_{fl} in degassed solution
0.05	0.05	0.05
0.38	0.16	0.19
1.37	0.18	0.20
5.30	0.40	0.45
10.20	0.43	0.48
21.89	0.58	0.60
30.45	0.59	0.62
43.48	0.60	0.64

The apparent quantum yields of poly[4-Cl-PPO-co-styrene] with 0.05-4.48 mol % of 4-Cl-PPO content increase rapidly from the value of 0.05 to 0.40. Above 9.98 mol % of 4-Cl-PPO the apparent quantum yields increase only slowly. The quantum yields of the copolymers are now lower than of the parent compound, PPO, which has the quantum yield of 0.80 [44]. Therefore, the relative quantum yield can be calculated by divide the

apparent quantum yield with mol % of 4-Cl-PPO (Figure 4.9). From the graph, when mol % of 4-Cl-PPO increases, the [apparent ϕ_{fl}/ mol % of 4-Cl-PPO] ratio is decrease. The graph is not linear, therefore it is obvious that there are interactions between the phenyl and 4-Cl-PPO chromophores even at low concentrations.

The ϕ_{fl} of degassed solutions are mostly greater values than the ϕ_{fl} of air-saturated solutions. This is because the oxygen of the air have a quenching effect on the copolymer. The fluorescence spectra of deoxygenated and non-deoxygenated samples show different intensities in their spectra.

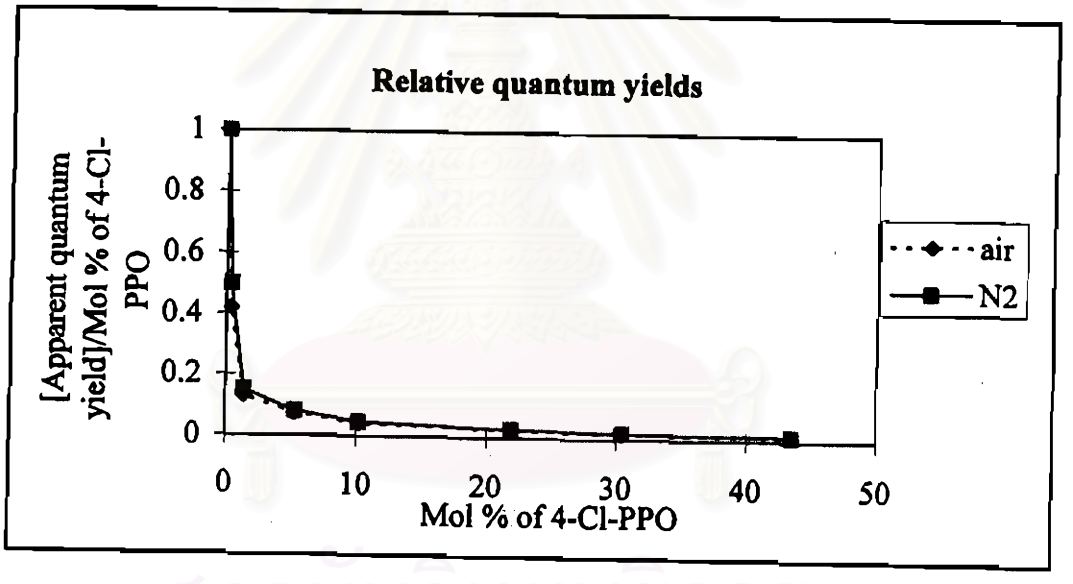


Figure 4.9 : [Apparent quantum yield/ mol % of 4-Cl-PPO] ratios vs. mol % of 4-Cl-PPO of poly[4-Cl-PPO-co-styrene]

The long chain and conformational properties of the copolymer result in the proximity of the chromophores, even in very dilute solution. This proximity can lead to interaction between the chromophores, leading to concentration quenching, energy transfer or excimer.