Chapter III

Experimental section

General Procedure

NMR spectra were recorded on a Bruker AC 200 MHz spectrometer. All samples were dissolved in chloroform-d_3 and the spectra were recorded relative to the tetramethyl silane peak in ppm of the applied field.

IR spectra were recorded on a Perkin Elmer 1710 spectrometer followed by Fourier transform of the data. Solid samples were obtained using KBr pellets, while liquid samples were held between NaCl plates.

UV Spectra were run on either a Hitachi U2000 spectrophotometer or a Perkin Elmer fast scan UV/VIS spectrophotometer with different concentrations of solutions in 1 cm path-length quartz cuvettes.

Emission spectra were recorded on a Perkin Elmer LS50 luminescence spectrophotometer with different concentrations of solutions in 1 cm path-length quartz cuvettes.

Purification of materials

1. Preparation of anhydrous diethyl ether

Diethyl ether (1 L) was heated with sodium metal (10 g) or benzophenone (10 g) under reflux until the dark blue or purple color persisted. The ether was then distilled immediately before use.

2. Preparation of dry carbon tetrachloride

Carbon tetrachloride was dried by simple distillation prior to use, rejecting the first 10 % of distillate, until the distillate was clear (bp. 77 ^{O}C).

3. Purification of styrene monomer

The *t*-butylcatechol (inhibitor) was removed from the styrene by washing twice with equal amounts of 10% NaOH solution. The styrene was washed with distilled water until litmus paper showed that the base had been all removed. The styrene was then dried over $CaCl_2$ and distilled under N_2 at about 42 °C and a pressure of 20 mm of mercury. The styrene was stored in a refrigerator for no more than twenty-four hours before use.

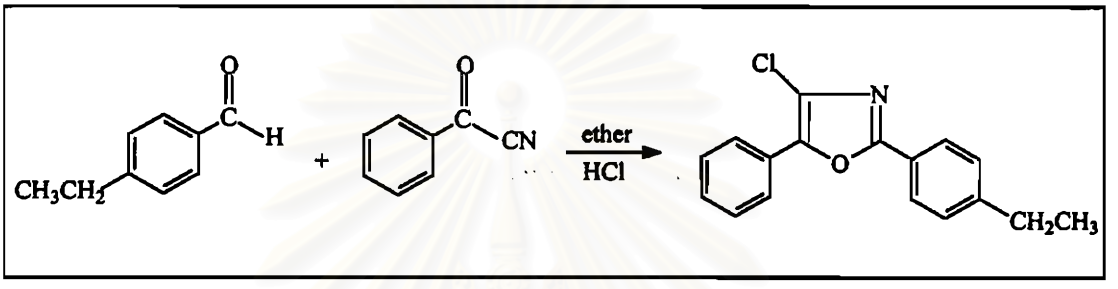
4. Purification of *N*-bromosuccinimide

NBS was recrystallized from 10 times its weight of hot water. The crystals were allowed to dry at room temperature in the dark.

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

The synthetic procedure of 4-chloro-2-(4′-vinylphenyl)-5-phenyl oxazole in shown in the following three steps.

1. 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole; 4-Cl-(Et)-PPO [25]



A solution of benzoyl cyanide (6.6 g, 50.0 mmol) in sodium dry diethyl ether (20 mL) was added dropwise, using an pressure-equilizing addition funnel with a $CaCl_2$ drying tube, into a solution of *p*-ethylbenzaldehyde (7.5 mL, 55.0 mmol) in diethyl ether (30 mL), while in a three necked flask which has been equipped with an inlet tube and outlet tube. The reaction flask was then connected to a HCl gas cylinder, the reaction mixture allowed to cool in an ice-NaCl cooling bath to 0 °C and then dry HCl gas passed into the solution in the reaction flask until the HCl gas was no longer absorbed by the reaction mixture (about two hours, tested by ammonia). At this stage, the reaction flask was quickly sealed, the stopper secured by wire and placed into the freezer compartment of the refrigerator overnight. The reaction mixture was then poured onto approximately 150 g of crushed ice with continuous stirring and extracted with ether (4x25 mL). The ether layer was washed with water (2x10 mL), saturated sodium bisulfite solution (2x10 mL) and then dried over magnesium sulfate. This was evaporated to dryness by rotary evaporation to

yield the crude product (10.4 g) as a pale yellow solid. The solid was then recrystallized from methanol to give 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole as colorless needles : mp 68-70 °C (lit[25] mp 70-71 °C); 9.64 g, 34.0 mmol, 68 %yield.

IR spectrum (KBr pellet) : 3018 (w, arom. C-H), 2962 (m, aliphatic C-H), 1580 (m, arom. C=C), 1490 (s, C=N), 1277, 1217 (m, C-Cl), cm^{-1}; (Fig. A1).

^{1}H-NMR spectrum ($CDCl_3$) : δ = 8.00-7.90 (m, 4H, arom.), 7.50-7.27 (m, 5H, arom.), 2.63 (q, J=7.5 Hz, 2H, $-CH_2-$), 1.24 (t, J=7.5 Hz, 3H, $-CH_3$) ppm; (Fig. A2).

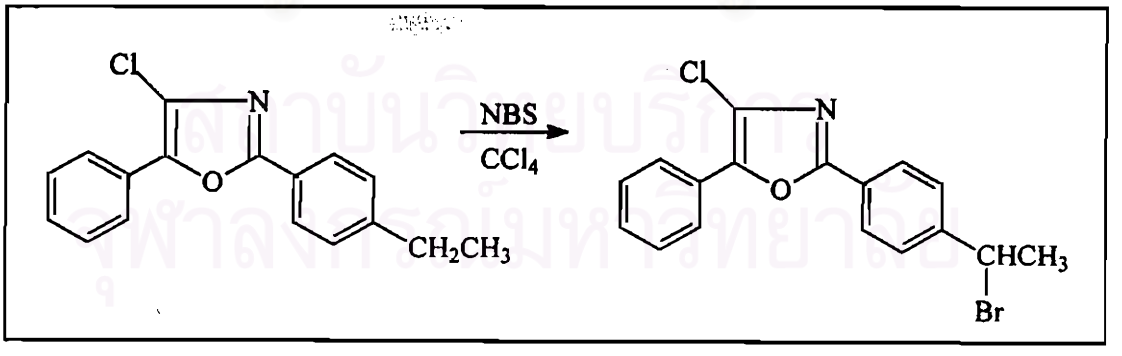
^{13}C-NMR spectrum ($CDCl_3$) : δ = 159.18 (oxazole C-2), 147.65 (oxazole C-5), 143.48 (oxazole C-4), 128.76-123.87 (arom. C), 28.86 ($-CH_2-$), 15.54 ($-CH_3$) ppm; (Fig. A3).

UV (CH_2Cl_2) : λ_{max} = 310 nm, log ε = 4.47; (Fig. A4).

Fluorescence excitation (CH_2Cl_2): λ_{max} = 312 nm (Fig. A5).

Fluorescence emission (CH_2Cl_2): λ_{max} = 370 nm

2. 4-chloro-2-4′-(α-bromoethyl)phenyl-5-phenyloxazole; 4-Cl-(Br-Et)-PPO



N-Bromosuccinimide (0.89 g, 5.00 mmol) and benzoyl peroxide (0.05 g, 0.2 mmol) were dissolved in freshly distilled carbon tetrachloride (15 mL). The solution was then added to 4-chloro-2-(4′-ethylphenyl)-5-

phenyloxazole (1.42 g, 5.00 mmol) in a 25-mL round bottom flask equipped with a condenser and a calcium chloride drying tube. The mixture was heated under reflux for one hour. The reaction mixture become yellow and a white precipitate separated. After this time, the mixture was allowed to cool to room temperature and the succinimide was removed by suction filtration. The filtrate was concentrated to dryness by rotary evaporation under vacuum. The yellow crude product (1.62 g) was subjected to flash column chromatography using silica gel (180 g). The column (30 x 5 cm.) was eluted with ethyl acetate-petroleum ether (2:5 v/v, 1500 mL), and 95 fractions (15 mL each) were collected. Fraction 25 to 50 were combined, evaporated and recrytallized from petroleum ether to give 4-chloro-2-4′-(α-bromoethyl)phenyl-5-phenyloxazole as white crystals : mp 81-83°C; 1.30 g, 3.6 mmol, 72 %yield.

IR spectrum (KBr pellet) : 3032 (w, arom. C-H), 2972 (m, aliphatic C-H), 1581 (m, C=C), 1490 (s, C=N), 1210 (m, C-Cl), 592 (m, C-Br) ; (Fig. A6).

^{1}H-NMR spectrum ($CDCl_3$) : δ = 8.05-7.90 (m, 4H, arom.), 7.55-7.23 (m, 5H, arom.), 5.19 (q, J=6.9 Hz, 1H, -CHBr-), 2.04 (d, J=6.9 Hz, 3H, $-CH_3$) ppm; (Fig. A7).

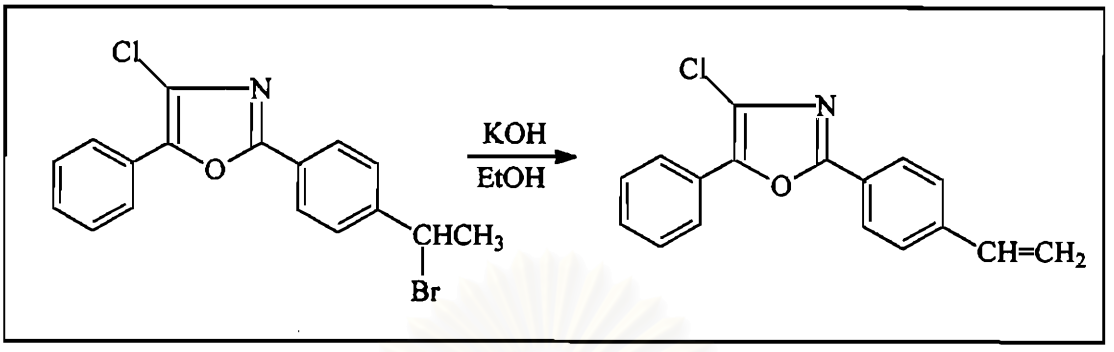
^{13}C-NMR spectrum ($CDCl_3$) : δ = 158.02 (oxazole C-2), 145.95 (oxazole C-5), 140.41 (oxazole C-4), 128.84-125.01 (arom.C), 48.29 (-CHBr-), 26.49 ($-CH_3$) ppm; (Fig. A8).

UV (CH_2Cl_2) : λ_{max} = 319 nm, $\log\varepsilon_{max}$ = 4.43; (Fig. A9).

Fluorescence excitation (CH_2Cl_2): λ_{max} = 326 nm (Fig. A10).

Fluorescence emission (CH_2Cl_2): λ_{max} = 375, 390 nm

3. 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole; 4-Cl-(vinyl)-PPO



Potassium hydroxide (0.3 g, 5.0 mmol) was placed in a 25-mL round bottom flask and was dissolved in ethanol (5 mL) by heating to reflux. The solution was then cooled to 40°C. 4-Chloro-2-4′-(α-bromoethyl)phenyl-5-phenyloxazole (0.36 g, 1 mmol) and hydroquinone (2 mg) as an inhibitor were added to the solution. The mixture was heated to reflux under a nitrogen atmosphere for three hours. After this time, the solution was cooled to room temperature and poured onto approximately 25 g of crushed ice with continuous stirring. The cooled mixture was extracted with diethyl ether (4x10 mL), dried over magnesium sulfate and evaporated to dryness by rotary evaporation. The resulting crude vinyloxazole (0.28 g) was subjected to silica gel (60.0 g) flash column chromatography. The column (20 x 3 cm.) was eluted with dichloromethane and petroleum ether (2:1 v/v, 850 mL), and 55 fractions (15 mL each) were collected. Fraction 3 to 14 were combined and evaporated to give 0.19 g of pale yellow solid which was recrystallized from ethanol to give 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole as colorless crytalline solid : mp 64-66°C, 0.15 g, 0.53 mmol, 53 %yield.

IR spectrum (KBr pellet) : 3016 (w, arom. C-H), 2923 (s, aliphatic C-H), 1581 (m, C=C), 1494 (s, C=N), 1278, 1220 (s, C-Cl) cm^{-1}; (Fig. A11)

^{1}H-NMR spectrum ($CDCl_3$) : δ = 8.05-7.91 (m, 4H, arom.), 7.52-7.23 (m, 5H, arom.), 6.85-6.65 (m, 1H, -CH=), 5.89-5.27 (m, 2H, $=CH_2$) ppm; (Fig. A12).

^{13}C-NMR spectrum ($CDCl_3$) : δ = 158.81 (oxazole C-2), 149.49 (oxazole C-5), 143.86 (oxazole C-4), 136.97 (CH=), 128.83-125.00 (arom.C), 115.85 ($=CH_2$) ppm; (Fig. A13).

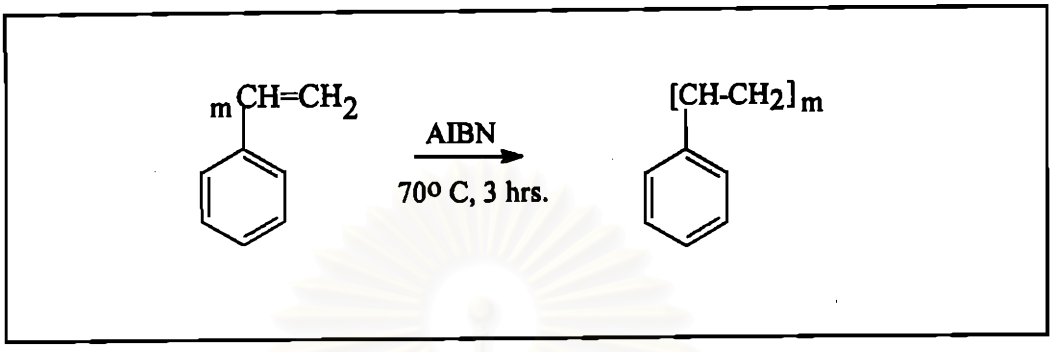
UV (CH_2Cl_2) : λ_{max} = 260 nm, $\log\varepsilon_{max}$ = 4.10; λ_{max} = 325 nm, $\log\varepsilon_{max}$ = 4.50; (Fig. A14).

Fluorescence excitation (CH_2Cl_2): λ_{max} = 260, 330 nm (Fig. A15).

Fluorescence emission (CH_2Cl_2): λ_{max} = 396 nm.

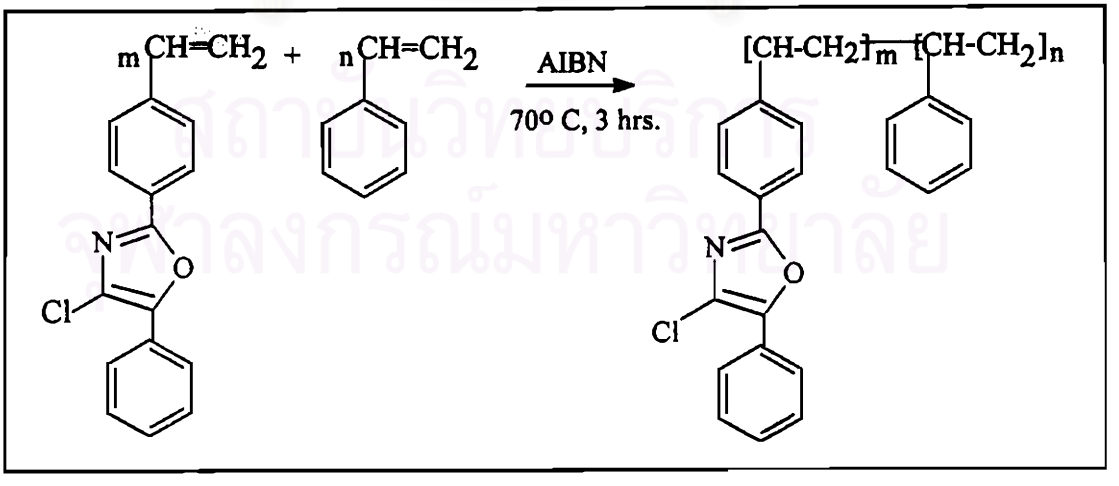
Part II : Synthesis of polymer

1. Preparation of polystyrene



Polystyrene was synthesized by using styrene (10 g) and 2,2′-azobis isobutyronitrile, AIBN (20 mg) as an initiator. The bulk polymerization process was carried out at 70 °C. Yield 6.4 g (64 %). The IR, UV absorption and fluorescence emission spectra of polystyrene are shown in Figures A16-A18, respectively.

2. Synthesis of poly[4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-styrene]; poly[4-Cl-PPO-co-styrene] by bulk radical polymerization



4-Chloro-2-(4′-vinylphenyl)-5-phenyloxazole and AIBN (20 mg) were placed into a large test tube (see Table 3.1). The tube was capped with a septum and flushed with nitrogen gas for 10 minutes. Distilled styrene was injected into the test tube by using a syringe. The tube was kept in an oil bath at a constant temperature of 70 °C and continuously stirred while purging with nitrogen for three hours. After this time, the mixture was removed from the oil bath and cooled quickly in dry ice. The tube was then opened and benzene (10 mL) added. The poly[4-Cl-PPO-co-styrene] was purified by precipitation 2 times using petroleum ether (10 mL each). The poly[4-Cl-PPO-co-styrene] precipitate was collected by suction filtration and dried at about 80 °C to give a pale yellow viscous solid.

Table 3.1 : The composition of poly[4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-styrene]

% 4-Cl-PPO feed	4-Cl-(vinyl)-PPO		styrene		copolymer weight
	(g)	mol	(mL)	mol	(g)
0.1%	0.03	9.6×10^{-5}	11.0	9.6×10^{-2}	1.45
1.0%	0.27	9.7×10^{-4}	11.0	9.6×10^{-2}	1.20
2.0%	0.05	1.8×10^{-4}	1.0	8.7×10^{-3}	0.44
5.0%	0.06	2.3×10^{-4}	0.5	4.3×10^{-3}	0.11
10.0%	0.14	4.8×10^{-4}	0.5	4.3×10^{-3}	0.24
25.0%	0.39	1.4×10^{-3}	0.5	4.3×10^{-3}	0.54
50.0%*	1.21	4.3×10^{-3}	0.5	4.3×10^{-3}	0.78
70.0%*	1.41	5.0×10^{-3}	0.25	2.2×10^{-3}	0.92

Note: Toluene 5 mL was added in reaction * as a solvent.

3. Film Preparation

Films were prepared from the poly[4-chloro-2-(4'-vinylphenyl)-5-phenyloxazole-co-styrene] by dissolving samples in toluene (10% w/v) and casting on glass plate. The solvent was evaporated slowly at room temperature (25 ^{0}C) over 1-2 hours, then the cast film was dried under vacuum for 12 hours.

4. Analysis of poly[4-chloro-2-(4'-vinylphenyl)-5-phenyloxazole-co-styrene] compositions

The feed compositions of each monomer mixture were varied to produce copolymers with variable nitrogen contents. Thus, the nitrogen content of each copolymer film was quantitated by elemental analysis from which value the incorporation of the 4-Cl-PPO moiety could be calculated. Table 3.2 illustrates the feed compositions, results of nitrogen analysis and copolymer compositions.

Table 3.2 : Determination of nitrogen in poly[4-chloro-2-(4'vinylphenyl)-5-phenyloxazole-co-styrene]

feed mol % 4-Cl-PPO	% $N_{calculate}$	% $N_{observed}$	mol % 4-Cl-PPO in copolymer
0.1	0.01	0.005	0.05
1	0.13	0.049	0.38
2	0.26	0.178	1.37
5	0.62	0.605	4.88
10	1.15	1.148	9.98
25	2.36	2.067	21.89
50	3.64	2.217	30.45
70	4.30	2.671	43.48

5. Synthesis of poly[4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-methyl methacrylate]; poly[4-Cl-PPO-co-MMA]

According to the synthesis of poly[4-Cl-PPO-co-styrene] method, this reaction used methyl methacrylate 0.23 mL (2.15 mmol) instead of styrene and 4-Cl-(vinyl)-PPO 0.61 g (2.15 mmol). Yield : 0.48 g. **Fluorescence emission** (Film): λ_{max} = 520 nm (Figure A33).

Part III : UV absorption and fluorescence emission analysis

All UV absorption spectra were recorded at wavelengths between 230-400 nm at room temperature (25°C) with air-saturated solutions. The fluorescence emission spectra were recorded at wavelengths between 270-600 nm with two excitation wavelengths at 260 and at 320 nm at room temperature (25 °C) with air-saturated or deoxygenated solutions. 1-cm pathlength quartz cuvettes were used for both UV and emission spectra. Plots of all UV absorption and fluorescence emission data are shown in Appendix B.

1. UV absorption and fluorescence analysis of poly[4-chloro-2-(4′-vinylphenyl)- 5-phenyloxazole-co-styrene] in dichloromethane solution

1.1 poly[4-Cl-PPO-co-styrene] 5 mg/100mL CH_2Cl_2

poly[4-Cl-PPO-co-styrene] solutions (with various mol ratios of the monomers) were prepared by dissolving 5 mg of the copolymer in dichloromethane in a 100-mL volumetric flask. The UV absorption spectra are shown in Figure A19. The fluorescence emission spectra of these copolymers were recorded at excitation wavelength of 260 nm in air-saturated solutions (Figure A20 and A21). Duplicate measurements did not differ by more than 10%.

1.2 poly[4-Cl-PPO-co-styrene] 1 mg/100mL CH_2Cl_2

The poly[4-Cl-PPO-co-styrene] solutions were prepared by diluting the stock solution (**1.1**) five-fold. UV absorption spectra of these diluted solutions were recorded (Figure A22). The copolymer solutions were analyzed by fluorescence emission spectroscopy at the excitation wavelength of 260 nm using air saturated and deoxygenated solutions (Figure A23 and A24). Fluorescence spectra of these copolymer solutions were recorded at an excitation wavelength of 320 nm using air-saturated solution (Figure A25). For clarity both the concentrations of 4-Cl-PPO in the copolymers and the mol ratios of the poly[4-Cl-PPO-co-styrene] are shown in Table 3.3.

Table 3.3 : The concentrations of 4-Cl-PPO in poly[4-Cl-PPO-co-styrene]

Mol % of 4-Cl-PPO	[4-Cl-PPO] in copolymer 5 mg/100 mL CH_2Cl_2, (M)	[4-Cl-PPO] in copolymer 1 mg/100 mL CH_2Cl_2,(M)
0.05	2.25×10^{-7}	4.50×10^{-8}
0.38	1.84×10^{-6}	3.68×10^{-7}
1.37	6.65×10^{-6}	1.33×10^{-6}
4.88	2.42×10^{-5}	4.84×10^{-6}
9.98	4.40×10^{-5}	8.80×10^{-6}
21.89	8.07×10^{-5}	1.61×10^{-5}
30.45	9.75×10^{-5}	1.95×10^{-5}
43.48	1.24×10^{-4}	2.48×10^{-5}

2. Fluorescence emission analysis of poly[4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-styrene] films.

Poly[4-Cl-PPO-co-styrene] films that were cast from 10% w/v toluene solution were analyzed by fluorescence emission spectroscopy with excitation wavelength at 260 nm. The normalized spectra are shown in Figure A26-A28.

Part IV : Fluorescence quantum yields of poly[4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-styrene]

Poly[4-Cl-PPO-co-styrene] were dissolved in dichloromethane and their concentrations were adjusted to provide the same absorbance at about 0.1 at 260 nm. These concentrations are sufficiently low to render the self quenching process unimportant. *p*-Xylene was used as a standard since the molecule also contains a benzene ring with quantum yield value is 0.33 [40].

The fluorescence emission spectra of the samples, air saturated and degassed solutions, were measured at the excitation wavelength of 260 nm at room temperature. The areas under the emission curve were recorded between 270-500 nm (Table 3.4 and 3.5). The quantum yields so measured were reproducible to within 10% or less from day to day.

Table 3.4 : Total area under the fluorescence emission curve of poly[4-chloro-2-(vinylphenyl)-5-phenyloxazole-co-styrene] in air-saturated solution (triplicates)

Mol % of 4-Cl-PPO	total area			average area
	(1)	(2)	(3)	
0.05	4878.54	4733.99	4753.54	4788.69
0.38	14569.14	14632.69	15100.85	14767.56
1.37	17515.54	17394.07	16716.63	17208.75
4.88	38567.89	37369.71	36339.74	37425.78
9.98	41026.85	41136.66	39514.60	40559.37
21.89	55020.05	53115.43	54474.77	54023.42
30.45	55223.24	54164.97	54874.06	54754.09
43.48	54902.59	54764.31	55731.00	555132.63

Table 3.5 : Total area under the fluorescence emission curve of the poly[4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-styrene] in deoxygenated-solution (triplicates)

Mol % of 4-Cl-PPO	total area			average area
	(1)	(2)	(3)	
0.05	5388..20	5384.76	5495.48	5422.56
0.38	17652.63	17876.69	17815.30	17781.54
1.37	18676.99	18569.54	18607.53	18618.02
4.88	41683.73	40212.53	42974.35	41623.54
9.98	45411.18	45570.66	44089.34	45023.70
21.89	57790.16	55710.72	56115.67	56539.00
30.45	58644.99	58103.66	58432.21	58393.62
43.48	59170.20	60402.14	595513.67	59969.53