อัตราส่วนความว่องไวของ 4-คลอโร-2-(4′-ไวนิลฟีนิล)-5-ฟีนิลออกซาโซล และเมทิลเมทาคริเลตสำหรับโคพอลิเมอไรเซชัน

นางสาวธิดารัตน์ หิรัญวิริยะ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

REACTIVITY RATIOS OF 4-CHLORO-2-(4′-VINYLPHENYL)-5-PHENYLOXAZOLE AND METHYL METHACRYLATE FOR COPOLYMERIZATION

MISS DHIDARATANA HIRUNVIRIYA

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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By Miss Dhidaratana Hirunviriya
Program Petrochemistry and Polymer Science
Thesis Advisor Associate Professor Supawan Tantayanon, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master’s Degree.

……………………………………….Dean of Faculty of Science
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นางสาวธิดารัตน์ หิรัญวิริยะ : อัตราส่วนความว่องไวของ 4-คลอโร-2-(4′-ไวนิลฟีนิล)-5-ฟีนิลออกซาโซลและเมทิลเมทาคริเลตสำหรับโคพอลิเมอไรเซชัน (REACTIVITY RATIOS OF 4-CHLORO-2-(4′-VINYLPHENYL)-5-PHENYLOXAZOLE AND METHYL METHACRYLATE FOR COPOLYMERIZATION)

อาจารย์ที่ปรึกษา : รศ. ดร.ศุภวรรณ ตันตยานนท์, อาจารย์ที่ปรึกษาร่วม, 80 หน้า. ISBN 974-346-759-9

4-คลอโร-2-(4′-เอทิลฟีนิล)-5-ฟีนิลออกซาโซล สามารถเตรียมได้จากปฏิกิริยาระหว่างพารา-เอทิลเบนซัลดีไฮด์และเบนโซอิลไซยาไนด์ในสารละลายเททราไฮโดรฟิวแรน ที่อิ่มตัวด้วยแก๊สไฮโดรเจนคลอโรด์ โบรมิเนชันของสารดังกล่าวโดยเอ็น-โบรโมซัคซินิมีด แล้วทำดีไฮโดรโบรมิเนชันโดยใช้โซเดียมเทอร์เทียรีบิวทอกไซด์ ได้4-คลอโร-2-(4′-ไวนิลฟีนิล)-5-ฟีนิลออกซาโซล

ได้สังเคราะห์พอลิ[4-คลอโร-2-(4′-ไวนิลฟีนิล)-5-ฟีนิลออกซาโซล-โค-เมทิลเมทาคริเลต] ที่มีสัดส่วนของมอนอเมอร์ต่างๆกัน โดยใช้วิธีพอลิเมอไรเซชันแบบสารละลายในโทลูอีน ที่อุณหภูมิ 50±1 องศาเซลเซียส และมีเอไอบีเอ็นเป็นตัวริเริ่มปฏิกิริยา โคพอลิเมอร์ที่เกิดน้อยกว่า 10% คอนเวอร์ชัน ในอัตราส่วนต่างๆ ในโทลูอีน ถูกวิเคราะห์โดยแก๊สโครมาโทกราฟีและพิสูจน์เอกลักษณ์โดยเอ็นเอ็มอาร์สเปกโทรสโกปี ค่าอัตราส่วนความว่องไวของมอนอเมอร์ถูกหาโดยวิธี Fineman-Ross ได้เป็น $r_{\text{4-Cl-(vinyl)-PPO}} = 1.07$ และ $r_{MMA} = 0.38$

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ภาควิชา…………………………………………… **ลายมือชื่อนิสิต**………………………………………..
สาขาวิชา………………………………………….. **ลายมือชื่ออาจารย์ที่ปรึกษา**……………………………
ปีการศึกษา…………………………………………..

##4072276923 PETROCHEMISTRY AND POLYMER SCIENCE
OXAZOLE / METHYL METHACRYLATE / REACTIVITY RATIOS / FINEMAN-ROSS / SCINTILLATOR
DHIDARATANA HIRUNVIRIYA : REACTIVITY RATIOS OF 4-CHLORO-2-(4′-VINYLPHENYL)-5-PHENYLOZAXOLE AND METHYL METHACRYLATE FOR COPOLYMERIZATION
THESIS ADVISOR : ASSOC. PROF. SUPAWAN TANTAYANON, Ph. D.
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The reaction between *p*-ethylbenzaldehyde and benzoyl cyanide in a tetrahydrofuran solution saturated with hydrogen chloride gas gave 4-chloro-2-(4′-ethylphenyl)-5-phenylozaxole. Its bromination by *N*-bromosuccinimide followed by dehydrobromination with sodium *t*-butoxide gave 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole.

Poly[4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-methyl methacrylate] at different monomer ratios was synthesized using solution copolymerization in toluene at 50±1 °C. AIBN was used as the initiator. The various copolymer ratios in toluene to give conversion less than 10% have been analyzed by gas chromatography and characterized by NMR spectroscopy. The monomer reactivity ratios were determined by Fineman-Ross method which give $r_{4\text{-}Cl\text{-}(vinyl)\text{-}PPO}$=1.07 and r_{MMA} = 0.38.

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Program...Student’s signature……………………….…….
Field of study......................................Advisor’s signature…………………………..
Academic year………………………..

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ABBRAVIATIONS

4-Cl-(Et)-PPO	4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole
4-Cl-(BrEt)-PPO	4-chloro-2-4′(α-bromoethylphenyl)-5-phenyloxazole
4-Cl-(vinyl)-PPO	4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole
MMA	methyl methacrylate
THF	tetrahydrofuran
CCl_4	carbon tetrachloride
NBS	N-bromosuccinimide
BPO	benzoyl peroxide
AIBN	2,2′-azobisisobutylonitrile
°C	degree Celsius
cm	centimeter
M	mole fraction in feed
m	mole fraction in copolymer
r	reactivity ratio

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Chapter I

Introduction

Scintillator is employed in scintillation counters to detect the several types of radiation. Generally, a counter consists of a scintillator, a photomultiplier tube converting the light flash into electrical impulses and an electronic device for counting these impulses as shown in Figure 1.1.

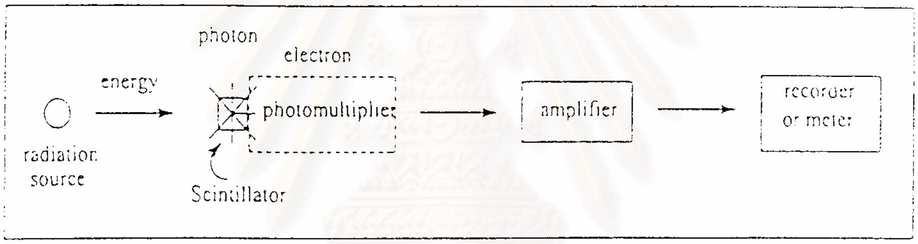

Figure 1.1 Schematic diagram of scintillation counter[1]

Historically , the first scintillators were single crystals such as antimony, sodium iodide, anthracene, naphthalene, *trans*-stilbene. Pure liquid e.g. *p*-xylene and pure plastics e.g. polystyrene were also used. Unfortunately, they exhibited low fluorescence intensities, thus their scintillation efficiency is too low for practical use.

A significant development has been the development of the binary system of liquid scintillators which contained one or more organic fluorescent compound(s) dissolved in an organic solvent system. The scintillator solutes are a selected class of compounds with a property of losing energy from their excited states in the form of light emission.

A common feature of efficient organic scintillator solute is aromatic ring linked in a manner to allow extended conjugation throughout the molecule. The aromatic ring systems which have been incorporated into scintillation solutes are phenyl, furan, pyrrole, oxazole, immidazole ring , etc.

Attempts to establish relationships between chemical structure and scintillation ability focus on the following requirements[2]:

-how to obtain fluorescence spectra at longer wavelengths.

-how to incorporate heterocyclic ring systems(such as oxazole) with better stability and sensitivity.

-structure – activity relationships found that : methyl, fluoro, and chloro substituent groups cause no difficulty and bromo, iodo, and hydroxyl show undesirable heavy atom effects.

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In efforts to improve upon the existing liquid scintillator counting and to provide data which would help to correlate chemical structure with the ability of various solutes to scintillate, a large number of organic compounds have been investigated [3,4]. *p*-Terphenyl in *p*-xylene was first proposed as a liquid scintillator in 1950[2]. Other chemicals which are often used as scintillator solutes are naphthalene, biphenyl, carbazole, 2,5-diphenyloxazole, anthracene, diphenylene oxide, etc. The solvent used in the system is usually aromatic such as benzene, toluene, and *p*-xylene which also provide effective transfer of excitation energy to the scintillator solute.The energy transfer can occur in two ways ; to another fluorescent molecule or to the solvent.Therefore the emission and efficiency of the liquid scintillator is influenced by the concentration of the fluorescent solute, the temperature and the viscosity of the solvent.

The development of plastic scintillators was prompted by advances in physics and the needs for computerized three dimensional scintillation counting. Plastic scintillators usually consist of an organic fluorescent compound mixed with polymer.

The advantage of plastic scintillator :

- producing a short emission of light (~10^{-9} sec.) and can be used in a broader range of temperatures than liquid scintillators. Since the polymer has a higher fluorescence quantum efficiency than the liquid solvent, there is an appreciable (10-20 %) component of radiative transfer resulting in higher fluorescence intensity than that of the liquid scintillator.

- the diffusion effect is not present in plastic systems.

- can be made into a variety of sizes and shapes such as thin film, rod, plate or cylinder.

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The problem of plastic scintillators is the migration of the fluorescent compound to the plastic surface. Thus, the scintillator have lower efficiency with use. To solve this problem, the copolymerization of scintillator solute with a monomer was carried out in order to bind it to the polymer.

Plastic scintillators[5]

Plastis scintillators represent a complex system composed of a polymer (polymer base) and an organic fluorescent compound(fluorescent additive). The main caracteristics of plastic scintillators are their scintillation efficiency and light yield.

The scintillation efficiency of the polymeric compound depends on the properties of both the fluorescent additives and the polymer base. The use of polymer in scintillation compounds is determined by their ability to convert excited energy into light energy, which happens because of the presence of the π-conjugated system in the macromolecule. The main requirement imposed on fluorescent additives is a high quantum yield.

The first plastic scintillators were produced on the basis of polystyrene and *p*-terphenyl in1950. The purpose of further investigations was to increase the scintillation efficiency of plastic scintillator by suitable selection of fluorescent additives and the polymer base. A large number of organic luminophore such as

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polyphenyls, aromatic condensed ring compounds, phenyl substituted derivatives of ethylene and diene and heterocyclic compounds.

The most promising is the application of the copolymer of given monomers either with styrene or methyl derivatives of styrene in the benzene ring or with methyl methacrylate. Of the inactive polymer bases, poly(methyl methacrylate) is most popular owing to its good physical and mechanical properties and high transmission. However, because of the absence in the repeating unit of PMMA of π-conjugation, PMMA based scintillators have low scintillation efficiency, not exceeding 10% compared with that of polystyrene. The light yield of inactive bases is increased by introducing a secoundary solvent. Satisfactory results are obtained with such secoundary solvent as naphthalene and phenanthrene. However, the light yield of large scintillator based on PMMA is no less than that polystyrene based scintillator.

Synthesis of 2,5-diaryloxazole

2,5-Diaryloxazole, such as 2,5-diphenyloxazole (PPO) is the most efficient fluorescent compounds which can be used as scintillators. The scintillators should be synthesized with absolute purity as even minute impurities can cause significant quenching of fluorescence emission.

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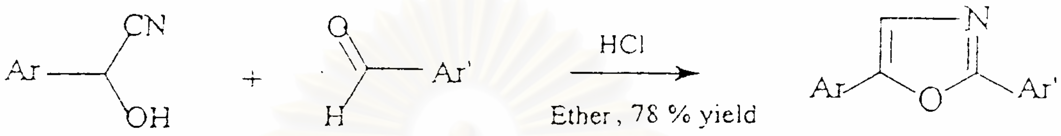
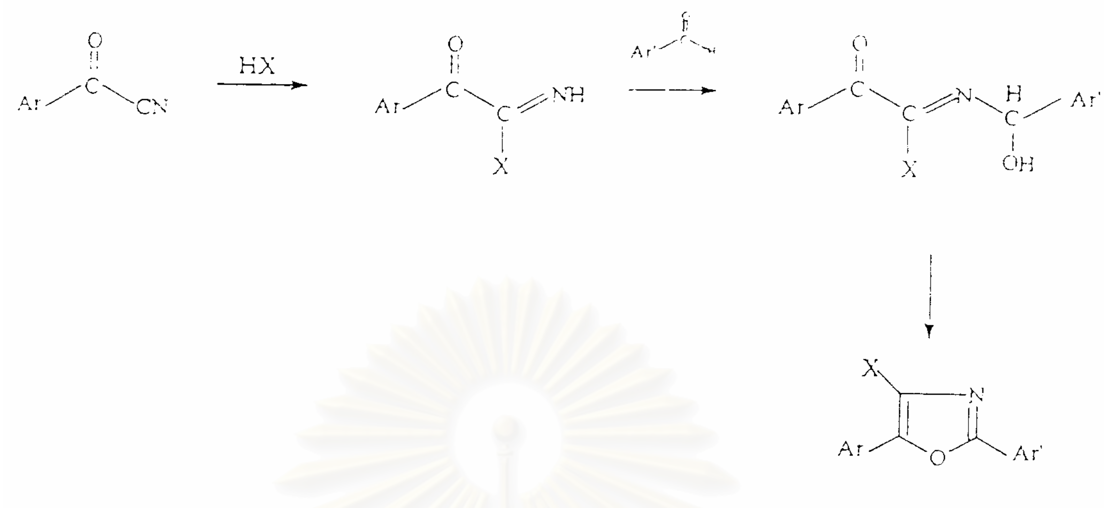
In general, 2,5-diaryloxazoles has been widely prepared by **the Fischer synthesis** from the one step reaction between an aryl cyanohydrin and an arylaldehyde in absolute ether at 0°C with dry hydrogen chloride [6,7].



The reaction always gives 2,5-diaryl-oxazolid-4-one as the main byproduct together with other heterocyclic colored compound. The yield of this byproduct amounts to half of the yield of the oxazole under optimal conditions, while in the presence of even traces of water the yield of the oxazole drops rapidly with increased yield of the oxazolid-4-one. There is also a certain ambiguity in that the starting materials may exchange hydrogen cyanide, thus causing scrambling of the phenyl ring in the product if this bears different substituents.

In 1963, a modification of the Fischer synthesis using an aroyl cyanide instead of cyanohydrins had been developed which yielded 2,5-diaryl-4-chloro(or bromo)oxazoles [8]. This method is led to the oxazoles in high yields (typically twice the yield of the analogue Fischer method) without the formation of the corresponding oxazolid-4-ones. The mechanism of the reaction involves iminohalide intermediates as shown in Scheme 1.



Scheme1

The halogen in the 4-position (Cl, Br or F) can be easily removed by reduction with Na amalgam in ethanol. Due to the convenience of using stable starting materials, easy purification of the product, obtained in high yield, this method is used almost exclusively for the commercial production oxazole based scintillators.

Generally, the fluorescence quantum yield of scintillators containing a halogen are generally low due to the "heavy atom" effect. However, it has been stated that the chloro group causes no difficulty in scintillation counting [9].

This thesis reports the synthesis of 4′-chloro-2-(4-vinylphenyl)-5-phenyloxazole, its copolymerization with methyl methacrylate and determination of the monomer reactivity ratios.

Objectives of the research

The aim of this research is to synthesize a new copolymer of 4- chloro-2-(4′-vinylphenyl)-5-phenyloxazole and methyl methacrylate which can be used as an effective plastic scintillator. The fluorescence emission properties and the reactivity ratios of the copolymer were determinated.

Scope of the research

1. Synthesis of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole.
    1.1 Synthesis of 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole
    1.2 Bromination of 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole
    1.3 Dehydrobromination of 4-chloro-2-4′-(α-bromoethylphenyl) -5- phenyloxazole

2. Preparation of poly(4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole-co-methyl methacrylate) with various ratios of monomers.

3. Determination of the monomer reactivity ratios by Fineman and Ross method.

4. Investigation the absorption and fluorescence emission properties of the copolymer.

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Chapter II

Theoretical Consideration

1.Polymer photophysics[10-13]

The photophysics of synthetic polymers can be simplified by considering them to have similar properties in photophysical terms like their small molecule analogues. These can be treated in the conventional way with reference to a stage diagram of Jablonski [10]. There are three states which play dominant roles in the photophysical process of organic molecules. They are the ground (unexcited) state (S_0) with opposing spins paired in molecular orbitals, the lowest triplet state (T_1) with parallel spins, and the lowest excited singlet state (S_1) which is higher in energy than the corresponding triplet state.

1.1 Absorption

The absorption of light (i.e. photons) by organic polymer molecules results in the excitation of π- and n-valence electrons including the additional excitation by molecular vibration. Absorption processes are graphically presented by using **Jablonski state diagrams** (Figure 2.1). The energy level indicated corresponds to energy differences.

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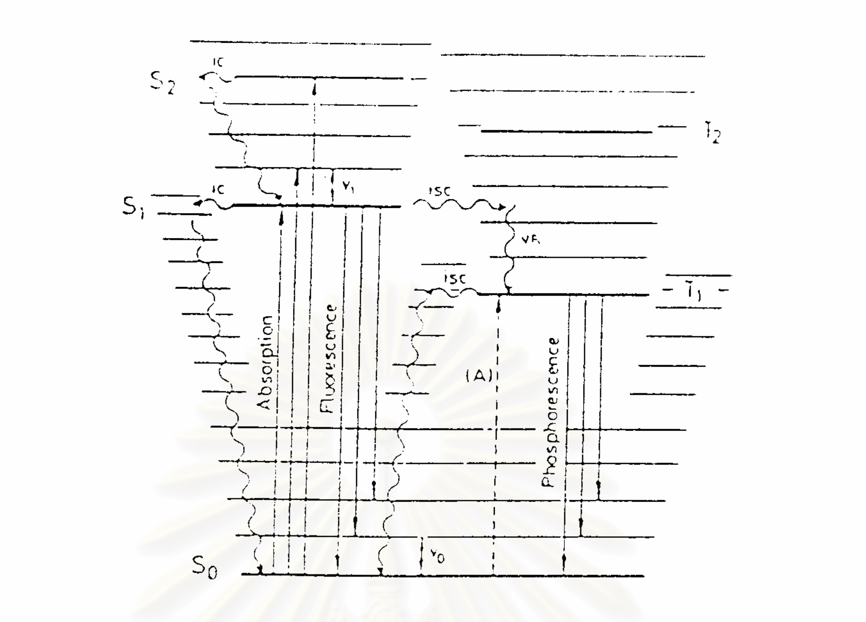

Figure 2.1 : Jablonski state diagram of energy levels of organic molecules

The processes are described by the Jablonski state diagrams in which states represented by horizontal lines are grouped into vertical columns according to their multiplicity. The individual processes are indicated by arrows (radiative process = straight arrow, non-radiative process = wavy arrows). The energy difference between the ground state (S_0), singlet states (S_1,S_0) and triplet states(T_1,T_2) are progressively lower at higher vibrational states. Each process is characterized by the rate constant (K_i); the sum of the reciprocal values of the deactivation rates of a vibrational state determines its lifetime (τ_i).

1.2 The molecular pathway

The reverse process to absorption, that is, the removal of the electron from the excited state back to the ground state, results in the emission of a photon. This

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process can occur via radiative transition which involves the spontaneous emission of a photon e.g. fluorescence and phosphorescence or radiationless transition e.g. internal conversion and intersystem crossing.

Radiative processes

Fluorescence is defined as the spin allowed emissive transition between vibrational states of identical multiplicity, usually from excitation of singlet S_1 to ground state S_0. The vibrational structure of fluorescence bands is a mirror image of the longer wavelength bands in the absorption spectrum, shifted to longer wavelengths. Fluorescence is comparatively fast with lifetimes usually in the range of 10^{-6}-10^{-4} sec. Because of the relatively short lifetime of fluorescence, the emission can be used to probe for a variety of interesting characteristics of polymers.

Phosphorescence is the spin forbidden emission of radiation between vibrational states of different multiplicity, generally from the T_1 state to the S_0 state. Since the T_1 state always lies below the S_1 state, this band occurs at longer wavelengths than that of fluorescence. The lifetimes are relatively long in the range of 10^{-4}-10 sec.

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Non-radiative process

There are two non-radiative processes. The first or **internal conversion**, denotes a radiationless transition between two electronic states of the same multiplicity, usually $S_n \rightarrow S_{n-1}$ or $T_n \rightarrow T_{n-1}$. In the specific case being considered, this would be the ground electronic state, and the transition would be denoted $S_1 \rightarrow S_0$. **Intersystem crossing** is a similar radiationless transition connected with a change in multiplicity (mostly $S_1 \rightarrow T_1$, $T_1 \rightarrow S_0$). Radiationless transitions are isoenergetic transition to a vibrationally excited lower electronic state, and followed by very rapid **vibrational relaxation** which occurs from any vibrational state and represents a return to the thermal equilibrium of the vibrational ground state within the same electronic state, for instance $S^v \rightarrow S$ or $T^v \rightarrow T$. This occurs in condensed systems by energy transfer, i.e. transfer of vibrational energy to the surrounding medium.

All processes discussed above, except simple vibrational relaxation, are unimolecular which can be illustrated with simple kinetic schemes presented in Table 2.1.

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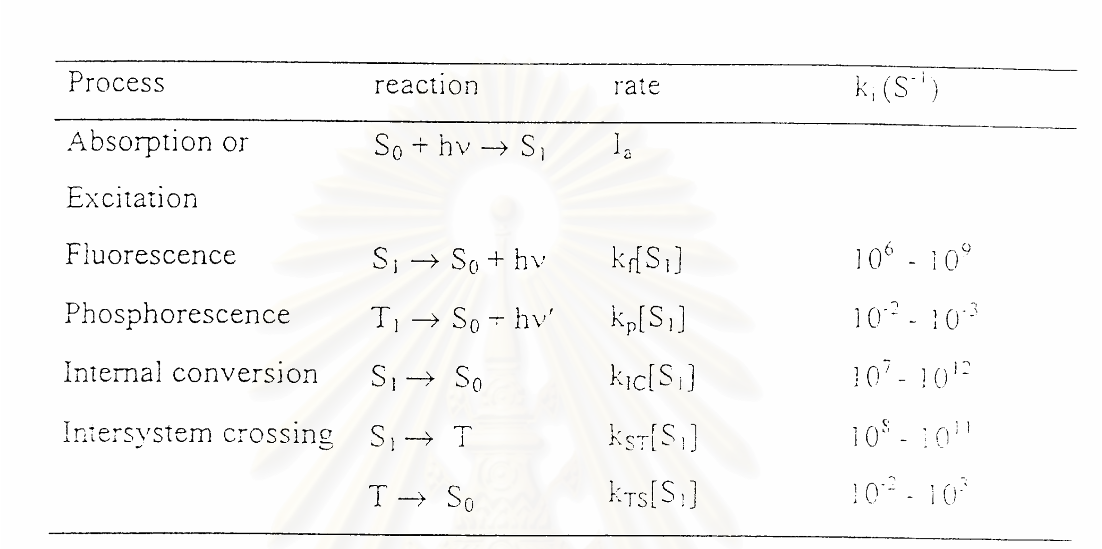
Table 2.1 The molecular pathways of photophysical process.



Process	reaction	rate	$k_i (S^{-1})$
Absorption or Excitation	$S_0 + h\nu \rightarrow S_1$	I_a	
Fluorescence	$S_1 \rightarrow S_0 + h\nu$	$k_f[S_1]$	$10^6 - 10^9$
Phosphorescence	$T_1 \rightarrow S_0 + h\nu'$	$k_p[S_1]$	$10^{-2} - 10^{-3}$
Internal conversion	$S_1 \rightarrow S_0$	$k_{IC}[S_1]$	$10^7 - 10^{12}$
Intersystem crossing	$S_1 \rightarrow T$	$k_{ST}[S_1]$	$10^8 - 10^{11}$
	$T \rightarrow S_0$	$k_{TS}[S_1]$	$10^{-2} - 10^3$

2. Determination of Monomer Reactivity ratios[14]

Most procedures for evaluating r_1 and r_2 involve the experimental determination of the copolymer composition for several different comonomer feed compositions in conjunction with the differential form of the copolymerization equation. Copolymerizations are carried out to as low degrees of conversion as possible (<10%) to minimize errors in the use of the differential equation. The copolymer composition is determined either directly by analysis of the copolymer feed or indirectly by analysis of comonomer feed. The copolymer compositions are analyzed by spectroscopy(IR, UV, NMR). Comonomer feed compositions are typically analyzed by high-pressure liquid chromatography(HPLC) or gas chromatography(GC).

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The method has been used to obtain monomer reactivity ratios from the copolymer composition data. The most often used method involves a rearrangement of the copolymer composition equation into a linear form in the monomer reactivity ratios. Fineman and Ross [15] rearranged the copolymer equation to

$$\boxed{G = r_1F - r_2}$$

Where $G = X(Y-1)/Y$, $F = X^2/Y$, $X = [M_1] / [M_2]$, $Y = d[M_1] / d[M_2]$. G is plotted against F to yield a straight line with slope r_1 and intercept r_2.

3. Types of Copolymerization Behavior

Different types of copolymerization behavior are observed depending on the values of the reactivity ratios. Copolymerizations can be classified into three types based on whether the product of the two monomer reactivity ratios r_1r_2 is unity, less than unity, or greater than unity.

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3.1 Random copolymerization : $r_1r_2 = 1$ or $r_1>1, r_2<1$ or $r_1<1, r_2>1$

Random copolymerization occurs when the two types of propagating species M_1^* and M_2^* show the same preference for adding one or the other of the two monomers. Most ionic copolymerization (both anionic and cationic) are characterized by the random type of behavior.

When $r_1 = r_2 = 1$ the two monomers show equal reactivities toward both propagating species. The polymer composition is the same as the comonomer feed with a random placement of the two monomers along the copolymer chain. For the case where the two monomer reactivity ratios are different, that is, $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, one of the monomers is more reactive than the other toward both propagating species. The copolymer will contain a larger proportion of the more reactive monomer in random placement.

3.2 Alternating copolymerization : $r_1 = r_2 = 0$

When $r_1 = r_2 = 0$ (and $r_1r_2 = 0$), the two monomers enter into the copolymer in equimolar amounts in a nonrandom, alternating arrangement along the copolymer chian. Each of the two types of propagating species preferentially adds the other monomer, that is, M_1^* adds only M_2 and M_2^* adds only M_1. As the r_1r_2 product decreases from unity toward zero, there is an increasing tendency toward alternation. Perfect alternation occurs when r_1 and r_2 are both zero.

A special situation arises when one of the monomer reactivity ratios is much larger than the other. For the case of $r_1 >> r_2$ (that is, $r_1 >> 1$ and $r_2 << 1$), both types of propagating species preferentially add monomer M_1. There is a tendency toward

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consecutive homopolymerization of the two monomers. Monomer M_1 tends to homopolymerize until it is consumed ; monomer M_2 will subsequently homopolymerize.

3.3 Block copolymerization : $r_1 > 1$, $r_2 > 1$

If both r_1 and r_2 are greater than unity (that is $r_1 r_2 > 1$) there is a tendency to form a block copolymer in which there are blocks of both monomers in the chain. This type of behavior has been encountered only in a few copolymerizations initiated by coordination catalysts.

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Chapter III

Experimental section

General Procedure

NMR spectra were recorded on a Bruker AC 200 MHz spectrometer. Chloroform-*d* was used as solvent for all samples and the spectra were recorded relative to the tetramethyl silane peak in ppm of the applied field.

IR spectra were recorded on a Impact 410 spectrometer. Solid samples were obtained using KBr pellets, while liquid samples were held between NaCl plates.

Gas chromatography data were recorded on a GC-14B with different concentrations of solutions (0.5 μl). The flow rate is 200 cm^3/min in silica capillary column (dia. 0.5 mm).

Fluorescence emission spectra were recorded on a spectrofluorometer FP-777 with different concentrations of solutions in 1 cm path-length quartz cuvette.

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Purification of Materials

1. Preparation of anhydrous tetrahydrofuran.

Tetrahydrofuran (250 mL) was heated under reflux over calcium hydride. The solvent 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 percent of distillate, until the distillate is clear (bp. 77°C).

3. Preparation of sodium *tert*-butoxide

Place 10 ml of *tert*-butylalcohol in a 25-mL round-bottomed flask and introduce 0.2 g of clean sodium metal in small pieces and warm under reflux until all the sodium has reacted about 2 hours.

4. Purification of *N*-bromosuccinimide

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

5. Purification of methyl methacrylate monomer

The inhibitor was removed from the methyl methacrylate by washing twice with equal amounts of 10% NaOH solution. The methyl methacrylate was washed with distilled water until litmus paper showed that the base had been all removed.

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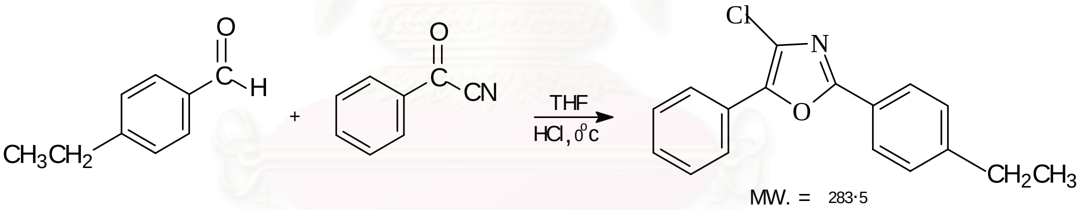
The methyl methacrylate was then dried over sodium sulphate anhydrous and evaporated under reduced pressure. The methyl methacrylate was stored in a refrigerator for no more than 24 hours before use.

<u>Part I</u> Preparation of 4-chloro-2-(4′- vinylphenyl)-5- Phenyloxazole

The synthetic procedure of 4-chloro-2-(4’- vinylphenyl)-5- phenyloxazole is show in the following three steps.

1. 4-chloro-2-(4′- ethylphenyl)-5-phenyloxazole ; 4-Cl-(Et)-PPO[8]



A solution of benzoyl cyanide (6.6 g, 50.0 mmol) and *p*-ethylbenzaldehyde (7.5 mL, 55.0 mmol) in 50 mL of dry tetrahydrofuran was contained in reaction flask. The reaction flask was then connected to a HCl gas cylinder, the reaction mixture was 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 2 hours, tested by ammonia). At this stage, the

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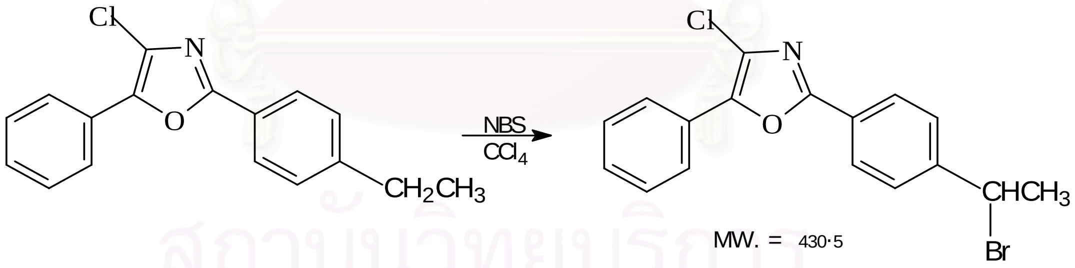
reaction flask was quickly sealed, the stopper secured by wire and placed into the freezer compartment of the refrigerator overnight. The reaction mixture was then poured onto approximately 150 g of crushed ice with continuous stirring and extracted with dichloromethane (4x25 mL). The dichloromethane 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. The crude product (11.74 g) was a pale yellow viscous liquid. The viscous liquid was recrystallized from methanol to give 4-chloro-2-(4′- ethylphenyl)-5-phenyloxazole as colorless needles : mp 74.5-75.5 °C ; 10.34 g , 36.47 mmol , 73 % yield.

2. 4-chloro-2-4′-(α-bromoethylphenyl)-5-phenyloxazole ; 4-Cl-(BrEt)-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

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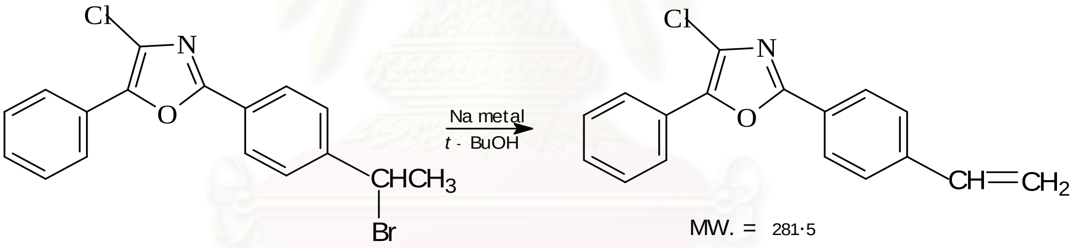
became orange and a white precipitate separated. After this time, the mixture was allowed to cool to room temperature and the succinimide was removed by suction filtration. The filtrate was concentrated to dryness by rotary evaporation under vacuum to give 4-chloro-2-4'-(α-bromoethyl)phenyl-5-phenyloxazole as pale yellow solid which was recrystallized from hexane to give 4-chloro-2-4'-(α-bromoethyl) phenyl-5-phenyloxazole as yellow crystals : mp 82-84 °C ; 1.77 g , 4.11 mmol , 82.51 % yield

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



Sodium *tert*-butoxide was prepared in *tert*-butanol. 4-chloro-2-(4'-bromoethyl)phenyl-5-phenyloxazole (0.72 g, 1 mmol) was added to the solution. The mixture was heated to reflux for three hours. After this time, the solution was cooled to room temperature and poured onto approximately 25 g of crush ice with continuous stirring. The cooled mixture was extracted with methylene chloride (4x20 mL), the methylene chloride layer was washed with water (2x20 mL) and then dried over sodium sulfate anhydrous. This was dried by rotary evaporation to give 0.54 g

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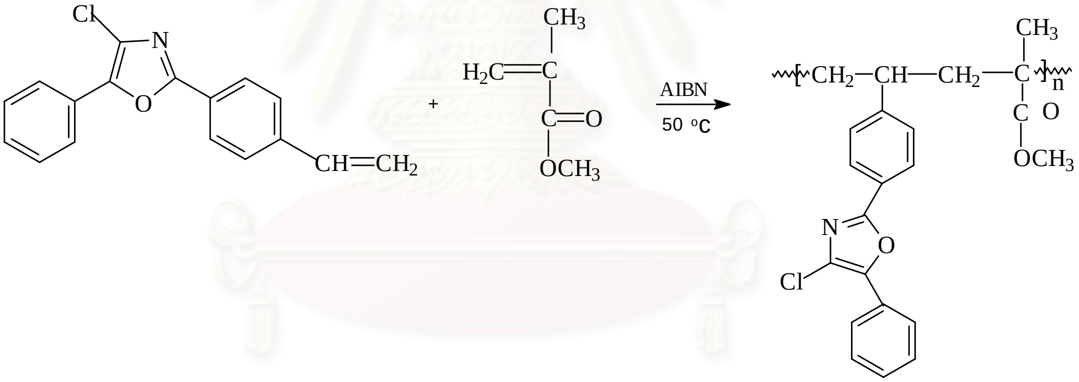
the pale yellow solid which was recrystallized from ethanol to give 4-chloro-2-(4’-vinylphenyl)-5-phenyloxazole as yellow crystals : mp 120-122 °C ; 0.48 g , 1.705 mmol , 85.71% yield.

<u>Part II</u> Synthesis of polymer

1. Synthesis of poly[4-chloro-2(4′-vinylphenyl)-5-phenyloxazole-co-methyl methacrylate] ; by solution polymerization.



4-chloro-2(4·-vinylphenyl)-5-phenyloxazole and distilled methyl methacrylate in toluene and AIBN were taken in a glass tube. The tube was capped with a septum and flushed with nitrogen gas for 10 minutes. The polymerizations of 4-chloro-2(4·-vinylphenyl)-5-phenyloxazole with methyl methacrylate were carried out in solution at 50°C by varying the feed ratios in monomers (Table 3.1). The initiator content was

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fixed at 0.53 molar percent to monomers. The reaction was stopped at a conversion of <10% by precipitating the copolymer in hexane.

Table 3.1 : The composition of poly[4-chloro-2(4·-vinylphenyl)-5-phenyloxazole-co-methyl methacrylate]

4-Cl-(vinyl)-PPO	MMA	$f_{4\text{-Cl-(vinyl)-PPO}}$	f_{MMA}
0.01	0.09	0.1	0.9
0.03	0.07	0.3	0.7
0.06	0.04	0.6	0.4
0.07	0.03	0.7	0.3
0.08	0.02	0.8	0.2
0.09	0.01	0.9	0.1

$f_{\text{4-Cl-(vinyl)PPO}}$ and f_{MMA} are the mole fractions of 4-chloro-2(4´-vinylphenyl)-5-phenyloxazole and methyl methyl methacrylate monomers in the feed.

<u>Part III</u> The determination of copolymer compositions by gas chromatography.

The feeds compositions of each monomer mixture were varried to produce copolymers .The composition of each copolymer was determined by gas chromatography. The copolymer mixture (0.5 μl) was injected at injection port temperature 265 °C, detection port temperature 275 °C and the column oven was working in temperature program which consists of the initial temperature, initial time, program rate, final temperature and final time as in Figure 3.1.

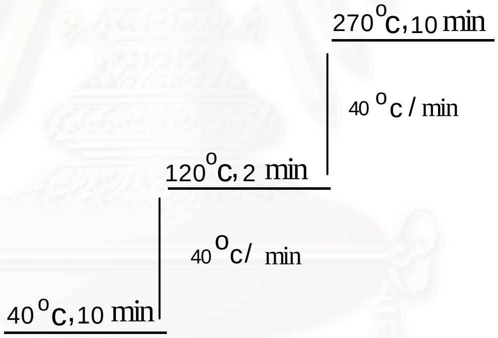

Figure 3.1 The temperature program of column oven

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Part IV Fluorescence Emission Analysis

The fluorescence emision spectra were recorded at 300-600 nm. with excitation wavelength at 260 nm at room temperature (25°C) with chloroform solutions. 1-cm pathlength quartz cuvettes were used for emission spectra. The dilute 4-Cl-(vinyl)-PPO and poly[4-Cl-(vinyl)-PPO-co-MMA] solutions of 1mg in 100 mL of chloroform and 11×10^{-2} mg in 10 mL of chloroform, respectively, was analyzed.

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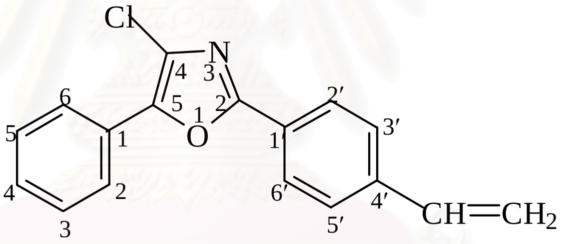
Chapter IV

Results and Discussions

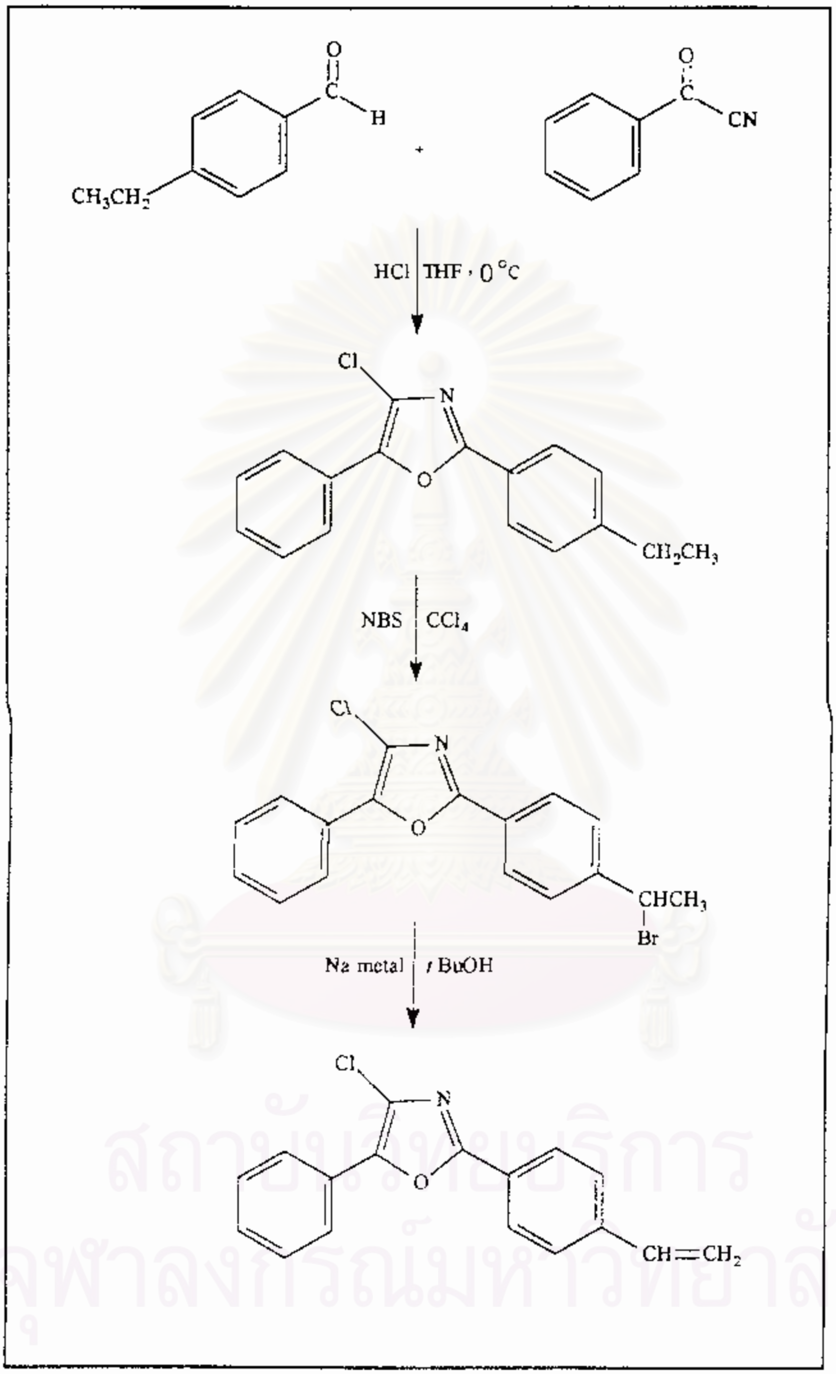
4.1 Synthesis of 4-Chloro-2-(4′-vinylphenyl)-5-phenyloxazole

The aim of this study is to synthesize 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole(1) for copolymerization with methyl methacrylate which is a new fluorescent polymer and determine the monomer reactivity ratios of both monomers. The chemical structure of (1) was shown below :



(1)

Scheme 4.1 shows the synthesis of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole which consists of 3 steps of reaction sequence. The synthetic route started from the synthesis of 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole by following the method of Ternai and Lakhan[8], which is the most efficient method due to the high yield and lack of by-products.



Scheme 4.1 The synthesis of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole

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4.1.1 Synthesis of 4-Chloro-2-(4′-ethylphenyl)-5-phenyloxazole

The first reaction involves the cyclization of benzoyl cyanide and *p*-ethylbenzaldehyde which is saturated with hydrogen chloride. The crude product was recrystallized from methanol to give colorless needle-like crystals (mp. 74.5-75.5°C) in 73%yield. Tetrahydrofuran (THF) had been used instead of diethyl ether which gave the product with higher than previously reported by Miss Athinee[17]. The ^{1}H NMR spectrum of 4-Cl-(Et)-PPO (Figure 4.1) in chloroform-*d* exhibits the characteristic absorption of the ethyl group as triplet at δ 1.26 (3H, t, J = 7.6 Hz) ppm coupled with a quartet at δ 2.69 (2H, q, J = 7.6 Hz) ppm. The chemical shifts of aromatic protons appear at δ 7.95 (5H,m) and 7.39 (4H,m) ppm.

The assignment of ^{13}C NMR spectrum of 4-Cl-(Et)-PPO (Figure 4.2) shows C-2, C-4 and C-5 of oxazole at 159.2, 143.5 and 147.6 ppm, respectively. The chemical shifts position of aromatic carbons appear at 123-128 ppm and that of ethyl group exhibits at 29.0 ppm and 15.5 ppm due to the $–CH_2$- and $–CH_3$.

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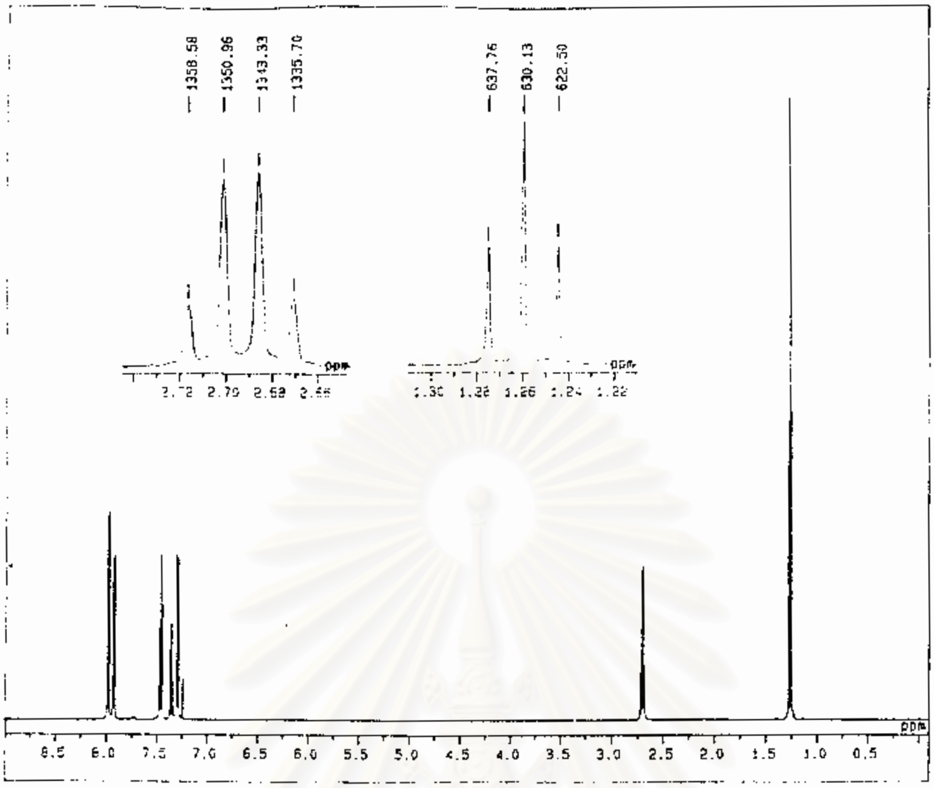

Figure 4.1 ^{1}H NMR spectrum of 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole ($CDCl_3$)

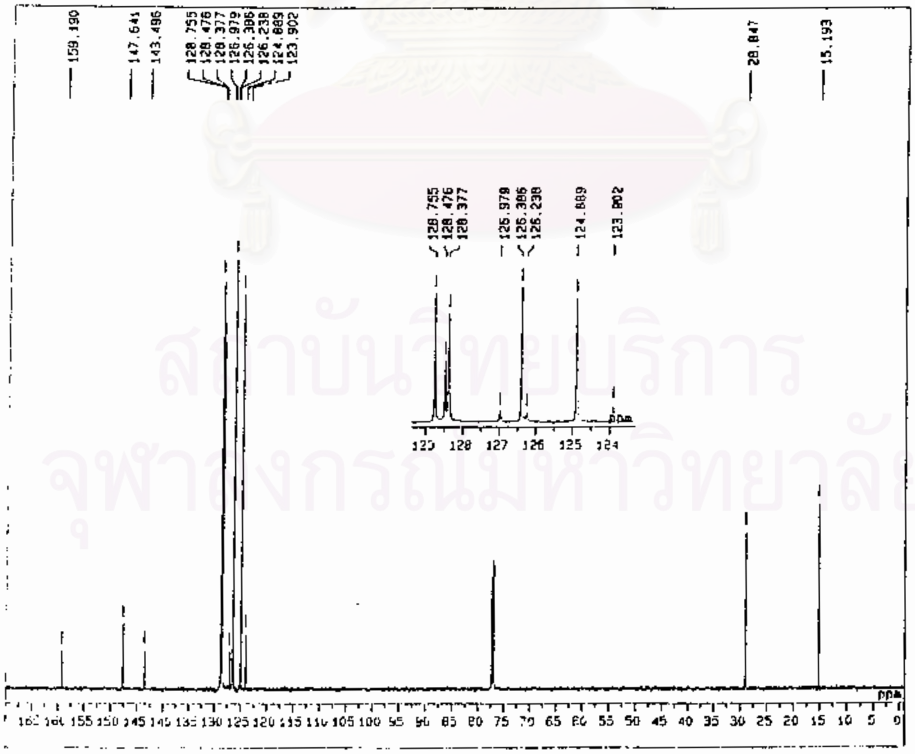

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Figure 4.2 ^{13}C NMR spectrum of 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole ($CDCl_3$)

The IR spectrum of 4-Cl-(Et)-PPO (Figure 4.3) shows aromatic C-H stretching at 3025 cm^{-1} and aliphatic C-H stretching at 2962 cm^{-1}. The absorption of C=N appears at 1497 cm^{-1}. The absorption of chloro compound appears at 1275 and 1219 cm^{-1} are due to C-Cl stretching. These peaks appear at about double the frequency normally designed to C-Cl stretching. The absorption peak at 1582 and 1614 cm^{-1} are assigned to the vibration arising from aromatic ring system. Accordingly, all data indicate that the product is 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole.

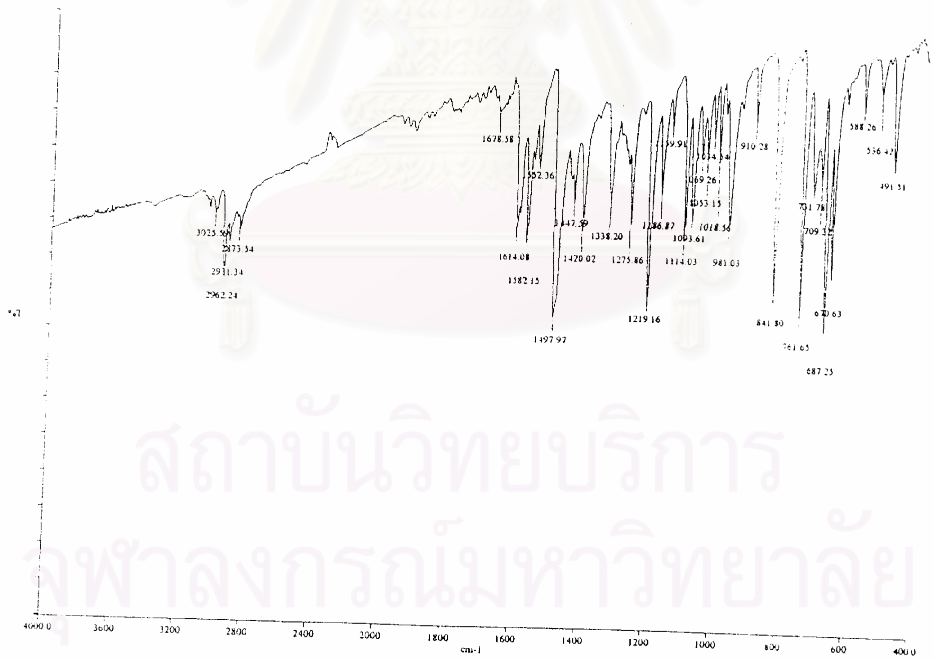

Figure 4.3 IR spectrum of 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole (KBr pellet)

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4.1.2 The Bromination of 4-Chloro-2-(4′-ethylphenyl)-5-vinyloxazole

The bromination of 4-Cl-(Et)-PPO was carried out using *N*-bromosuccinimide(NBS) and benzoyl peroxide(BPO) in carbon tetrachloride solution. This let to 4-chloro-2-4′-(α-bromoethylphenyl)-5-phenyloxazole [4-Cl-(BrEt)-PPO]. The crude product was recrystallized from hexane as yellow needle-like crystal (mp.=82-84°C)in 82.51 %yield. .The ^{1}H-NMR spectrum shows the bromoethyl protons at δ5.21 (1H, q, J = 7.0 Hz)ppm due to the –CHBr- and δ2.06 (3H, d, J = 7.0 Hz) ppm due to $–CH_3$ as shown in Figure 4.4.

The ^{13}C-NMR spectrum of 4-Cl-(BrEt)-PPO (Figure 4.5) exhibits signals of $–CH_3$ and –CHBr- at δ 26.4 and 48.2 ppm. The aromatic signals are at δ 125.0-128.8 ppm while the oxazole carbons show peaks at δ158.3 (C-2), 144.0 (C-4) and 158.3 (C-5) ppm.

The IR spectrum of 4-Cl-(BrEt)-PPO (Figure 4.6) looks similar to spectrum of 4-Cl-(Et)-PPO except the strong absorption at 593 cm^{-1} which is due to the C-Br stretching. Consequently, all spectroscopic data confirms the structure of 4-Cl-(BrEt)-PPO .

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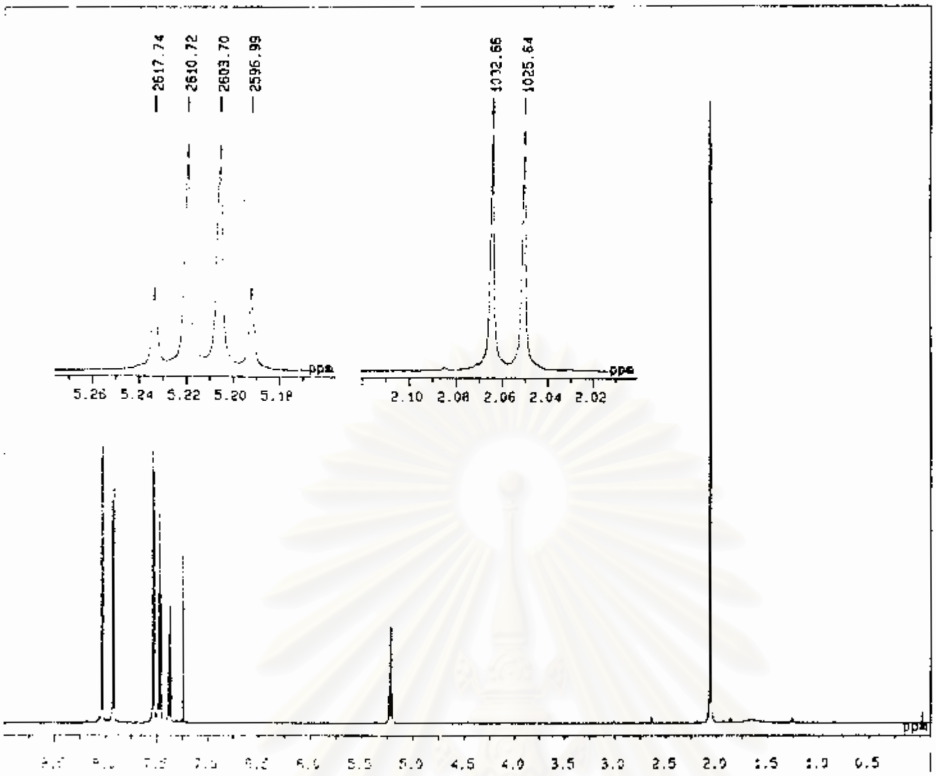

Figure 4.4 ^{1}H NMR spectrum of 4-chloro-2-4′-(α-bromoethylphenyl)-5-phenyloxazole(CDCl$_3$)

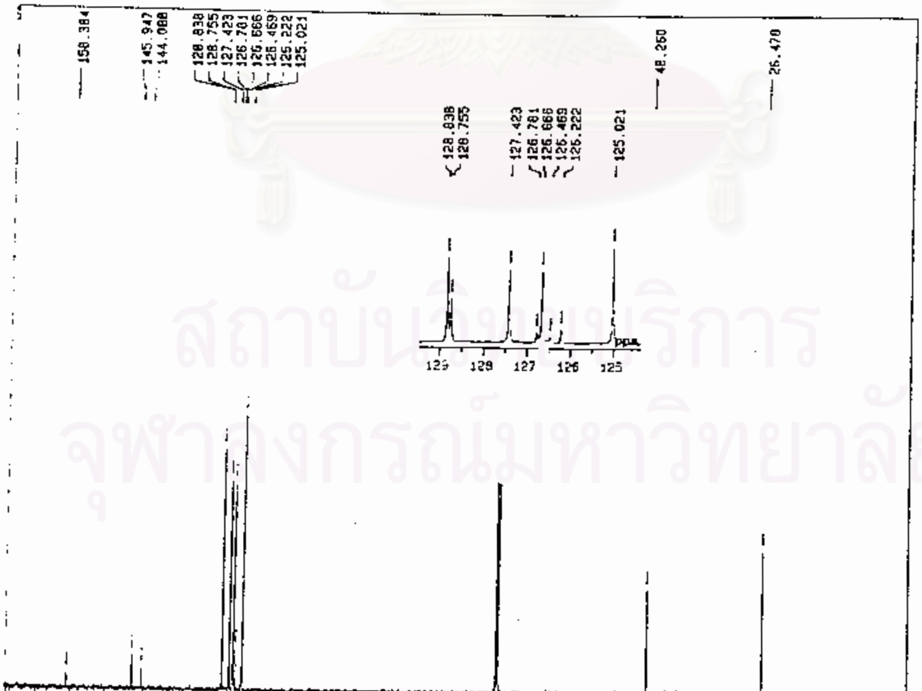

Figure 4.5 ^{13}C NMR spectrum of 4-chloro-2-4′-(α-bromoethylphenyl)-5-phenyloxazle(CDCl$_3$)

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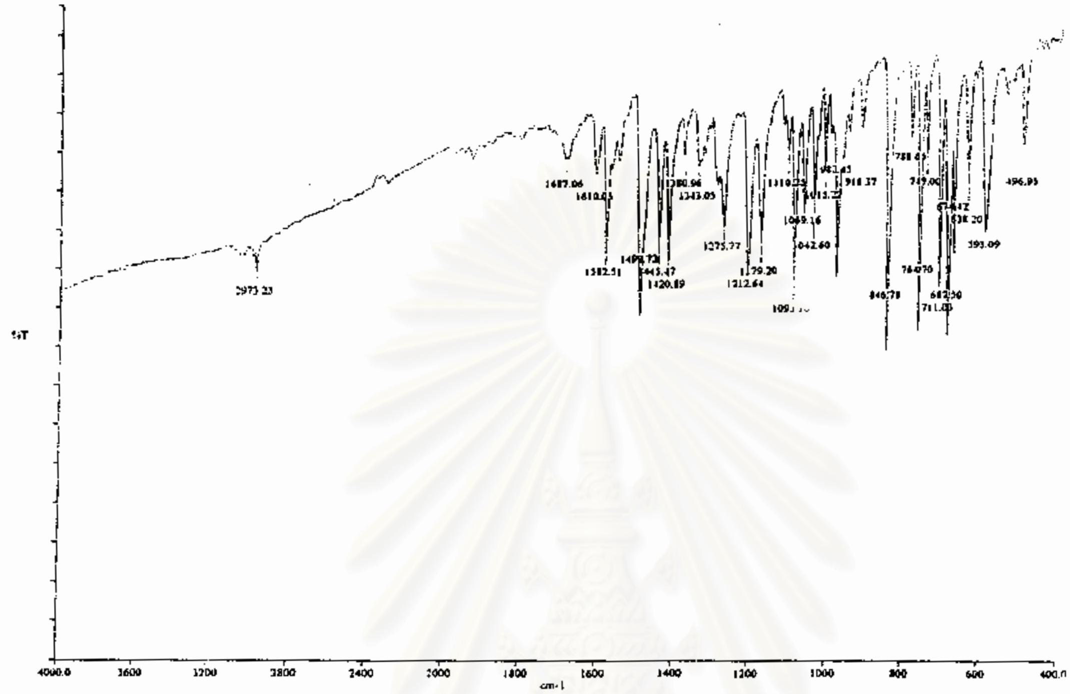

Figure 4.6 IR spectrum of 4-chloro-2-4′-(α-bromoethylphenyl)-5-phenyloxazole (KBr pellet)

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4.1.3 The Dehydrobromination of 4-Chloro-2-4′-(α-bromoethylphenyl) -5-phenyloxazole

4-Chloro-2-(4′-vinylphenyl)-5-phenyloxazole [4-Cl-(vinyl)-PPO] was prepared by nucleophilic attack on the bromoethyl compound. Firstly potassium hydroxide had been used and very low yield of the product was obtained. Therefore, the more bulky base was used in order to suppress the substitution reaction and enhance the yield of the product. It was found that the product was formed. The 4-Cl-(vinyl)-PPO was recrystallized from methanol as yellow crystal (mp.=120-122°C) in 85.71 %yield. The ^{1}H-NMR spectrum of 4-Cl-(vinyl)-PPO (Figure 4.7) exhibits peak at δ 6.74 (1H , dd, J = 10.9, 8.7Hz) ppm for –CH= and δ 5.85 (1H, dd, J = 17.0, 0.6 Hz) ppm and δ 5.35 (1H, dd, J = 10.3, 0.6) ppm for the $=CH_2$ trans- and cis- protons, respectively.

The ^{13}C-NMR of 4-Cl-(vinyl)-PPO (Figure 4.8) confirms the identity of the product, since the chemical shifts of -CH= appears at δ 135.9 ppm and $=CH_2$ at δ 115.8 ppm. The rest of spectrum is similar to 4-Cl-(Et)-PPO, except to absorption at δ 29.0 and 15.5 ppm which is due to ethyl group.

The IR spectram of 4-Cl-(vinyl)-PPO (Figure 4.9) reveals the absence of the peak at 593 cm^{-1}. This obviously illustrates the dehydrobromination of 4-Cl-(BrEt)-PPO and the formation of 4-Cl-(vinyl)-PPO.

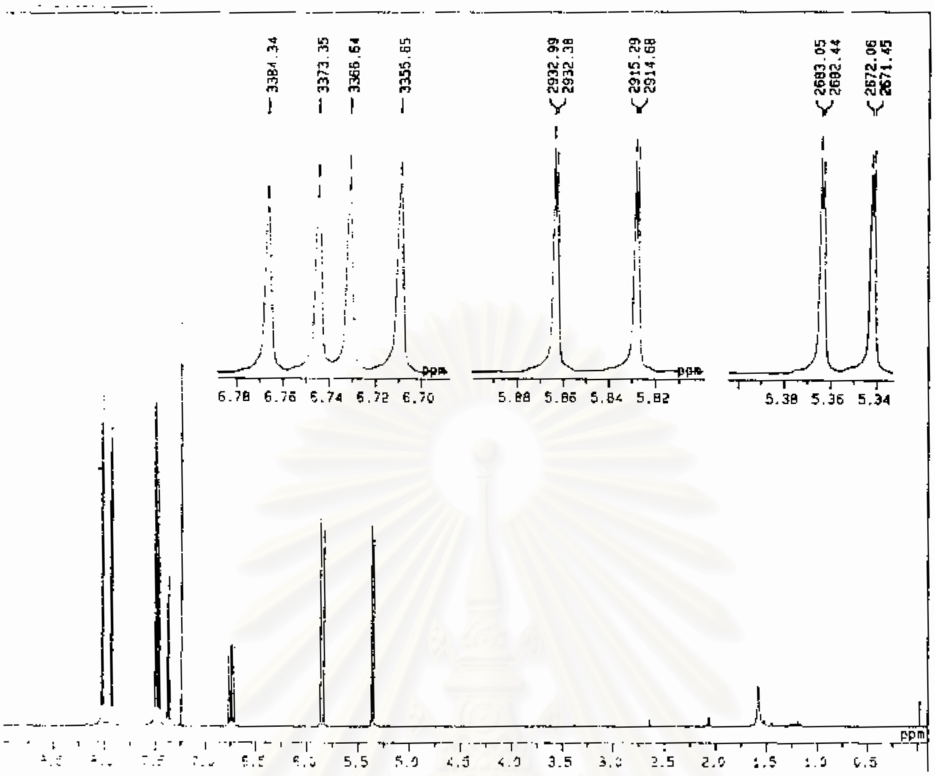

Figure 4.7 ^{1}H NMR spectrum of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole ($CDCl_3$)

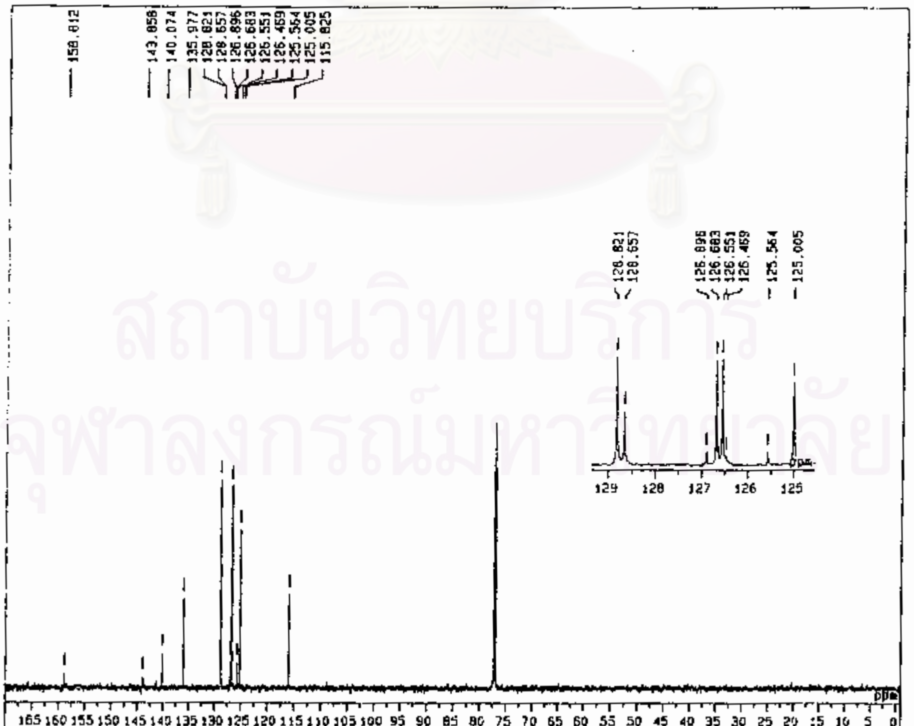

Figure 4.8 ^{13}C NMR spectrum of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole ($CDCl_3$)

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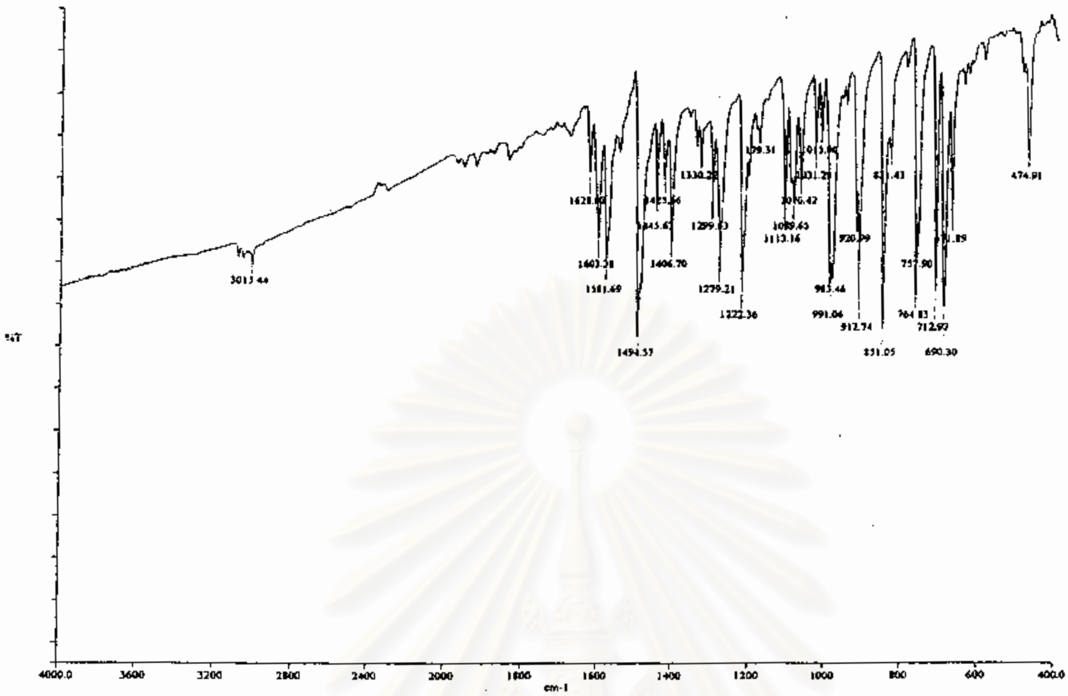

Figure 4.9 IR spectrum of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole (KBr pellet)

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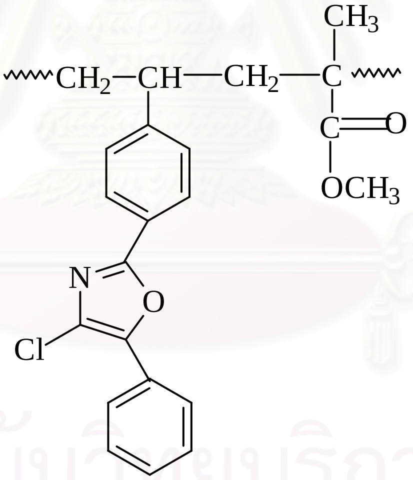
4.2 Synthesis of Poly[4-Cl-(vinyl)-PPO-co-MMA]

Copolymerization of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole[4-Cl-(vinyl)-PPO] with methyl methacrylate(MMA) was prepared by solution polymerization using AIBN as initiator in toluene. The copolymer was obtained as pale yellow solids which was soluble in aromatic and chlorinated solvents and insoluble in cyclohexane, methanol and water. They were characterized by ^{1}H-NMR and IR spectroscopy. The formula of poly[4-Cl-(vinyl)-PPO-co-MMA] is illustrated in Scheme 4.4.



Scheme 4.2 The structure of poly[4-Cl-(vinyl)-PPO-co-MMA]

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4.2.1 Structure Elucidation of Poly[4-Cl-(vinyl)-PPO-co-MMA]

^{1}H-NMR spectrum of poly[4-Cl-(vinyl)-PPO-co-MMA] (Figure 4.10) shows resonance absorption at 2.8 ppm and at 6.5-8.0 ppm due to the methylene proton and the aromatic protons of 4-Cl-(vinyl)-PPO , respectively. The methyl protons of ester give a broad peak at 3.5 ppm. The signals at 1.66 ppm is due to the methylene protons of the main chain. The broad signals at 0.7 ppm may be assigned to the α-methyl protons of MMA units. Disappearance of the absorption at 5.0-6.0 ppm indicates the polymerization of 4-Cl-(vinyl)-PPO and MMA and the purity of the product.

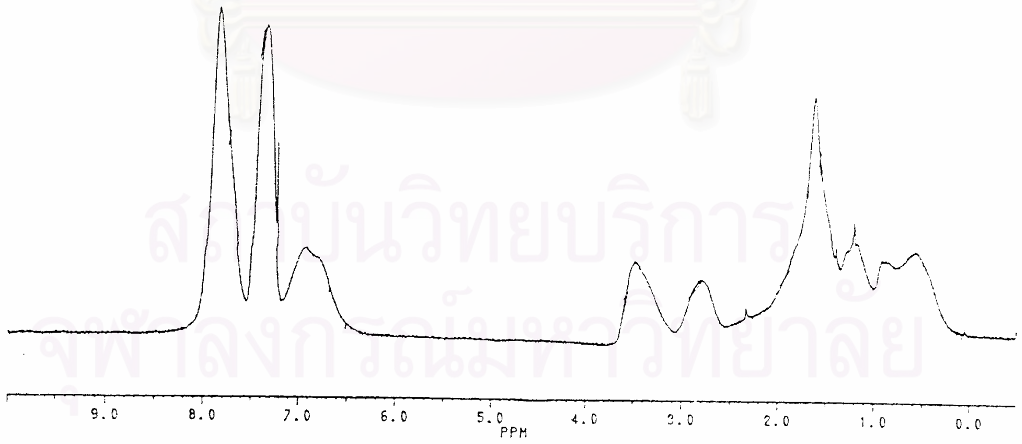

Figure 4.10 ^{1}H NMR spectrum of poly[4-Cl-(vinyl)-PPO-co-MMA] ($CDCl_3$)

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The IR spectrum of the copolymer appears at 1732 cm^{-1} due to the C=O stretching of ester carbonyl protons and at 1494 cm^{-1} due to the C=N stretching of 4-Cl-(vinyl)-PPO. These absorption are comparable to C=O stretching of MMA and C=N stretching of 4-Cl-(vinyl)-PPO as shown in Figures 4.11-4.12.

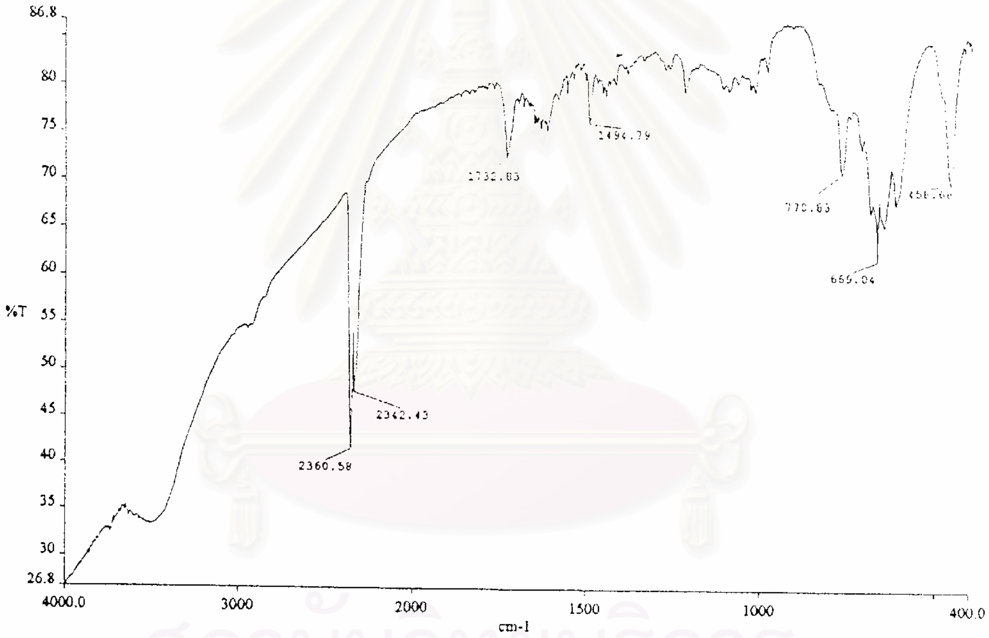

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Figure 4.11 IR spectrum of poly[4-Cl-(vinyl)-PPO-co-MMA] (KBr pellet)

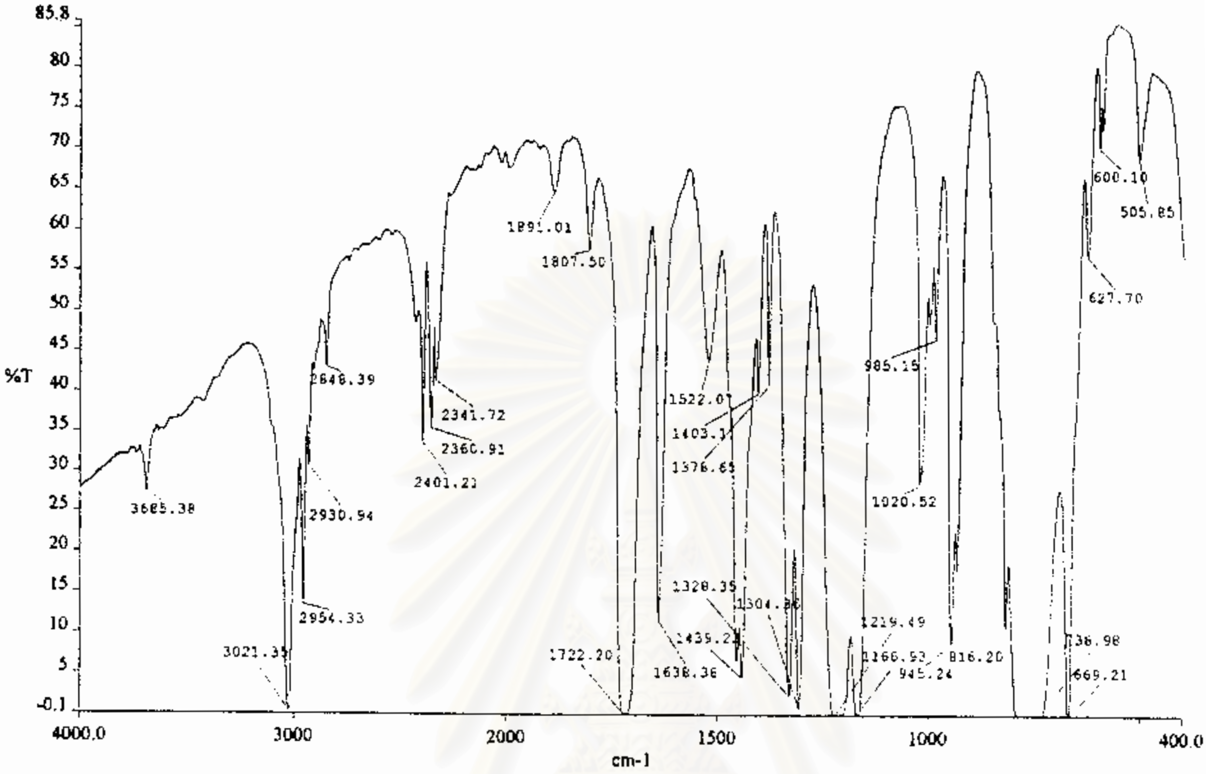

Figure 4.12 IR spectrum of methyl methacrylate ($CHCl_3$)

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4.2.2 Gas Chromatography of Copolymer

Copolymerization of 4-Cl-(vinyl)-PPO and MMA can be monitored by gas chromatography, by using gas chromatography at the condition described in experimental section. In this experiment, the solution of 4-Cl-(vinyl)-PPO and MMA was thus analyzed before and after reaction. From the copolymerization of 4-Cl-(vinyl)-PPO and MMA at the mole ratio of 3:7. 4-Cl-(vinyl)-PPO and MMA had different retention time, 3.7 and 24.1 min, respectively. The gas chrpmatogram showed the decrease in the peak height of both monomers after 30 minutes of the reaction as shown in Figure 4.13.

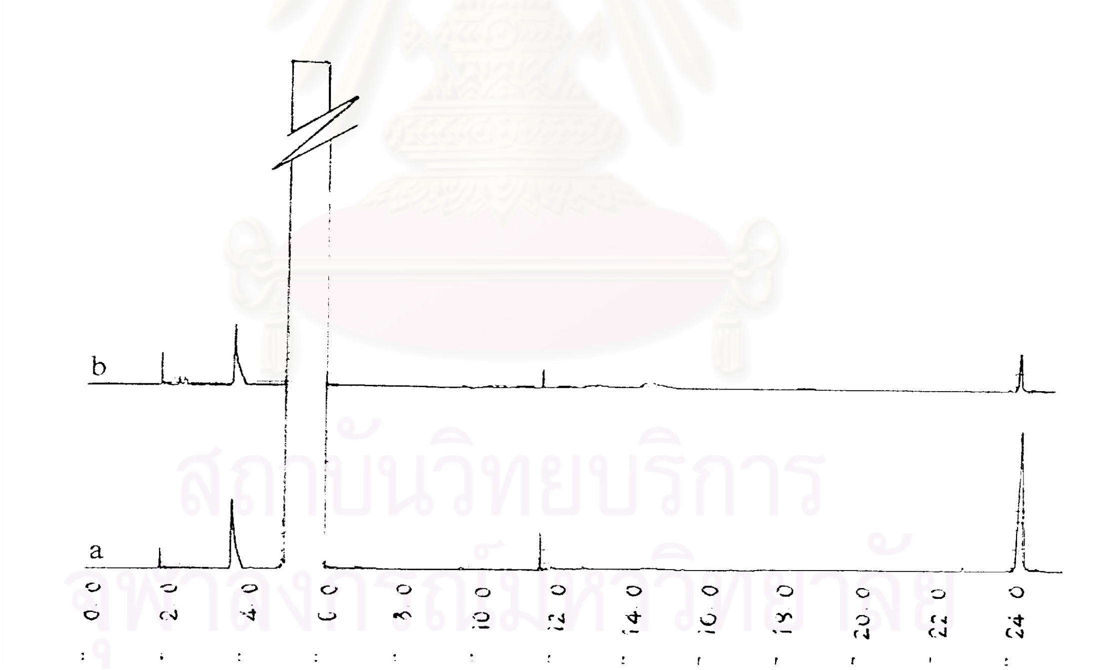

Figure 4.13 The typical gas chromatogram of the mixture of 4-Cl-(vinyl)-PPO and MMA in toluene (a) before and (b) after copolymerization.

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4.3 The Determination of Monomer Reactivity Ratios

The determination of the monomer reactivity ratios, copolymerizations were carried out to as low degree of conversion. The determination of suitable condition of copolymerization was considered from several factors, such as, time, temperature, amount of solvent, etc.

4.3.1 Investigation of Copolymerization at Low Conversion

The copolymerization of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole with methyl methacrylate at different mole ratios were carried out at 70°C with the reaction time of 22 min. The gas chromatography was used for analysis. The reduced peak area of each monomer was assumed that was the amount of incorporated monomers in copolymer. The degree of conversion in Table 4.1 was calculated by the below equation:

% conversion = (peak area of monomer feed – peak area of monomer at the
copolymerize time)x100 / peak area of monomer feed

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Table 4.1 The %conversion of copolymerization at 70°C ; t = 22 min.

Ratios (mmol)		% Conversion	
4-Cl-(vinyl)PPO	MMA	4-Cl-(vinyl)PPO	MMA
0.05	0.45	58.69	7.12
0.10	0.40	64.94	17.82
0.15	0.35	63.89	28.10
0.20	0.30	66.16	21.86
0.25	0.25	57.76	11.20
0.30	0.20	58.49	21.75
0.35	0.15	53.68	10.43
0.45	0.05	49.66	13.05

From Table 4.1, % conversion of every ratio is higher than 10% which indicated that all ratios used in the copolymerization have too long reaction time. Therefore, the reaction time could be reduced.

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4.3.2 Effecct of Time on the Copolymerization of 4-Cl-(vinyl)-PPO with MMA

The time range 0-15 minutes was used for copolymerization at 0.05:0.45 mole ratio of 4-Cl-(vinyl)-PPO and MMA with the reaction temperature of 70°C. The degree of conversion was shown in Table 4.2.

Table 4.2 The % conversion of the copolymerization at 70°C in various time.

Time (min)	% Conversion	
	4-Cl-(vinyl)PPO	MMA
0	-	-
2	28.14	17.06
5	44.19	21.23
7	41.84	22.37
10	48.35	22.40
15	51.47	25.88

From the % conversion of this condition it indicates that the copolymerization extended over 10%. Observing to the reaction time at 2 min, the percentage conversion is still much higher than 10% which may be occurred by effect of temperature.

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4.3.3 Effect of Temperature on the Copolymer of 4-Cl-(vinyl)-PPO with MMA

The suitable temperature must be considered with initiator which was azobisisobutylonitrile(AIBN). AIBN was commonly used at 40-70°C. Thus, the reaction temperature was selected at 50°C. The mole ratio of 4-Cl-(vinyl)-PPO and MMA was used at 1:1.

Table 4.3 The %conversion of the copolymerization at 50°C in various time

Time (min)	% Conversion	
	4-Cl-(vinyl)-PPO	MMA
0	-	-
1	3.56	0.38
2	2.89	1.76
5	14.87	9.87
7	18.05	14.31
10	23.21	14.36

From above data it was indicated that the copolymerization time at 1 and 2 min give the conversion less than 10% of both monomers. Thus, the suitable condition is about 1 or 2 min. Besides time and temperature, the amount of solvent may be involved.

4.3.4 Effect of the Amount of Solvent on Copolymerization of 4-Cl-(vinyl)-PPO with MMA

If the concentration influences to the reaction, high concentration will allow the collision of molecules more possibility than lower concentration. In this study toluene was used in different volume (1 mL and 3 mL). The reaction time range 0-10 was used on the mole ratio at 1:1 of 4-Cl-(vinyl)-PPO and MMA, respectively.

Table 4.4 The % conversion of copolymerization in toluene 1 mL and 3 mL in various time

Time(min)	% conversion in toluene 1 mL		% conversion in toluene 3 mL	
	4-Cl-(vinyl)-PPO	MMA	4-Cl-(vinyl)-PPO	MMA
0	-	-	-	-
1	2.31	1.61	4.02	4.99
2	4.47	3.15	16.64	9.94
5	12.13	10.23	24.16	13.27
7	14.99	12.69	31.54	24.42
10	18.84	15.25	50.71	28.86

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From Table 4.4, it was indicated that the concentration of solution not effective to the percentage of conversion because of toluene 1 mL gives %conversion less than 10 with reaction time of 1 and 2 min and 3 mL give % conversion less than 10 with the reaction time of 1 min. Therefore, the suitable condition for determining the monomer reactivity ratios was carried out at 50°C in toluene 1 mL in reaction time about 2 mins.

4.3.5 Copolymerization of 4-Chloro-2-(4′-vinylphenyl)-5-phenyloxazole with Methyl Methacrylate

Copolymers with various proportions of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole(4-Cl-(vinyl)-PPO) and methyl methacrylate (MMA) were prepared by radical polymerization in toluene solution using 2-2′-azobisisobutylonitrile as initiator at 50°C±1. The incorporatation of 4-Cl-(vinyl)-PPO and MMA in copolymers was determined by gas chromatography. The typical chromatogram of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole and methyl methacrylate in copolymer solutions was shown in Figure 4.13. There are five peaks in the chromatogram, i.e., AIBN peak, MMA peak, toluene peak, AIBN radical peak and 4-Cl-(vinyl)-PPO peak which had the retention time at 1.9, 3.8, 6.3, 11.8 and 24.6 , respectively.

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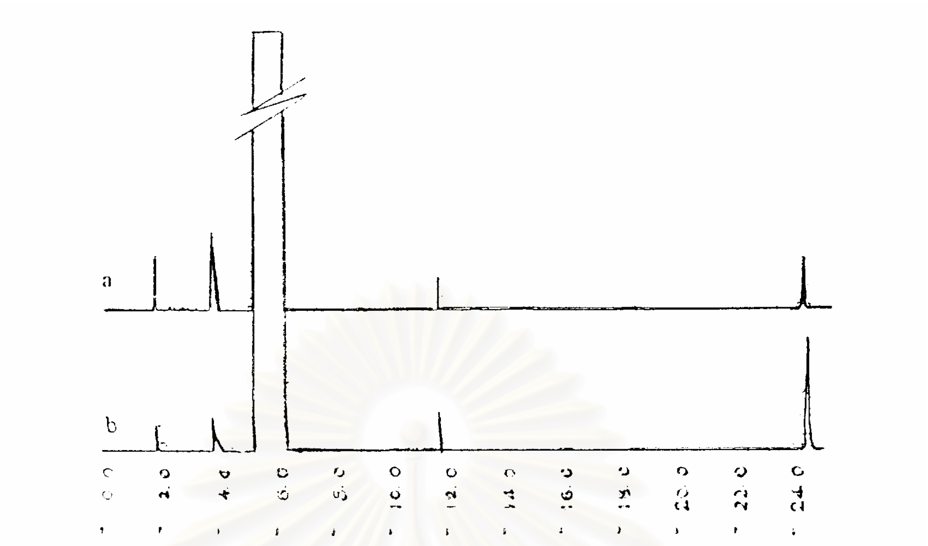

Figure 4.14 The chromatogram of copolymer solutions by gas chromatography in different mole ratios (a) 4-Cl-(vinyl)-PPO(0.03m.mol) : MMA(0.07m.mol) (b) 4-Cl-(vinyl)-PPO(0.07m.mol) : MMA(0.03m.mol)

The amount of monomers was represented by peak area of gas chromatogram . The peak area and % conversion of poly[4-Cl-(vinyl)-PPO-co-MMA] in six mole ratios and time were represented in the Appendix B. The composition of each copolymer was calculated from the linear equation of the calibration curve of 4-Cl-(vinyl)-PPO in Figure A1 and MMA in Figure A2. The calibration curves was plotted between peak area (Table 4.5) and the amount of monomer in the feed.

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Table 4.5 Peak area of 4-Cl-(vinyl)-PPO and MMA at t = o

Ratios of Monomer (mmol)	Peak Area	
4-Cl-(vinyl)-PPO : MMA	4-Cl-(vinyl)-PPO	MMA
0.01 : 0.09	10373.0	26021.5
0.03 : 0.07	16063.0	20436.5
0.06 : 0.04	32940.5	10730.0
0.07 : 0.03	33949.5	8024.0
0.08 : 0.02	38497.0	5148.5
0.09 : 0.01	40886.5	2422.0

4.3.6 Calculation of the Monomer Reactivity Ratios

The calibration curves (Figures A1-A2) are represented to yield the linear equation :

$$Y = 400760X + 6431.6 \qquad \text{for 4-Cl-(vinyl)-PPO}$$

and

$$Y = 297612X - 940.97 \qquad \text{for MMA}$$

X and Y are the concentration and the peak area of monomers, respectively.

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Both linear equations were used to determine the non polymerized monomer which indicated in the peak area and it was converted to concentration (Table 4.6).

Table 4.6 Peak Area of 4-Cl-(vinyl)-PPO and MMA at time less than 10% conversion

Ratios of Monomer (mmol)	Peak Area		Amount of Non-Copolymerize Monomer (mmol)	
4-Cl-PPO:MMA	4-Cl-PPO	MMA	4-Cl-PPO	MMA
0.01 : 0.09	9690.0	25546.5	0.008	0.089
0.03 : 0.07	15953.0	19296.5	0.023	0.068
0.06 : 0.04	28874.0	10552.5	0.056	0.039
0.07 : 0.03	32316.5	7898.0	0.065	0.029
0.08 : 0.02	36239.0	4819.5	0.074	0.019
0.09 : 0.01	37949.0	2308.5	0.079	0.009

Each monomer incorporated in the copolymer was assumed to be the converted monomer amount relative to the initial amount, revealed from the gas chromatography. Therefore, the incorporated monomer amounts in the copolymer in each mole ratio were shown in Table 4.7, which resulted in the copolymerization in various mole ratios and time (Appendices B1-1 to B1-6). The minimum time for less than 10% conversion of monomers was chosen.

The extent of incorporation of 4-Cl-(vinyl)-PPO and MMA into the poly[4-Cl-(vinyl)-PPO-co-MMA] was observed that the increasing of amount of monomer feed involves the increasing of incorporated monomer in copolymer.

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Table 4.7 Copolymerization of 4-chloro-2-(4-vinylphenyl)-5-phenyloxazole with methyl methacrylate

Monomer Feed 4-Cl-(vinyl)-PPO (mmol)	Monomer Feed MMA (mmol)	Mole Fraction of 4-Cl-(vinyl)-PPO in Copolymer (m_1)	Mole Fraction of MMA in Copolymer (m_2)	Reaction Time (min)	Conversion (%)	
					4-Cl-(vinyl)-PPO	MMA
0.01	0.09	0.667	0.333	2	6.58	1.80
0.03	0.07	0.777	0.222	2	0.68	5.57
0.06	0.04	0.800	0.200	1	9.22	1.65
0.07	0.03	0.833	0.167	1	4.81	1.57
0.08	0.02	0.857	0.143	1	5.86	5.63
0.09	0.01	0.917	0.083	1	7.18	4.68

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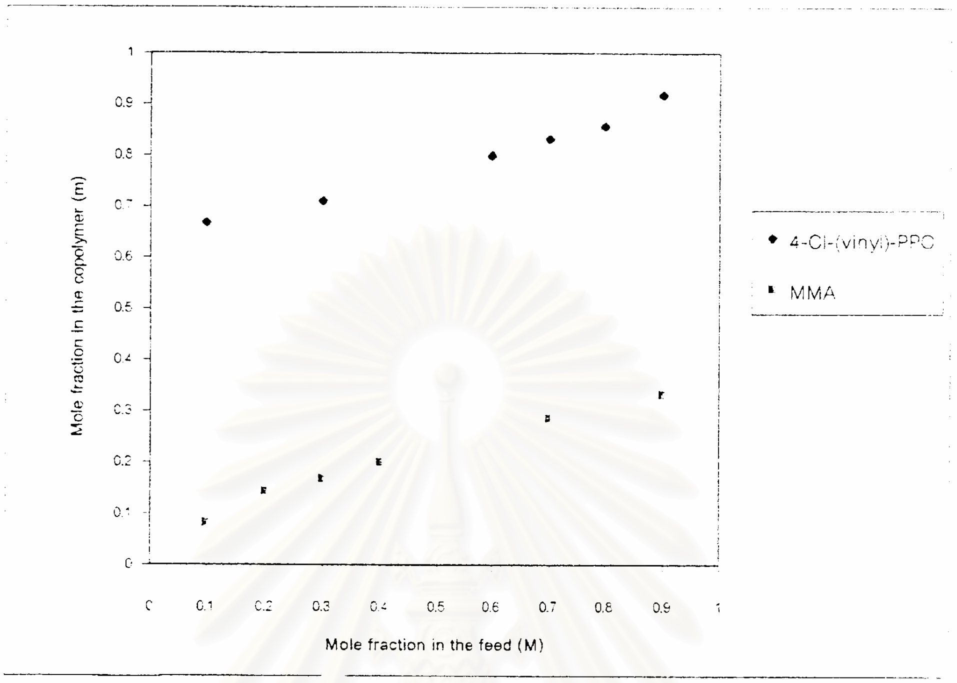

Figure 4.15 Monomer-copolymer composition curves of 4-Cl-(vinyl)-PPO-MMA copolymer systems. *M* = mole fraction of monomers in the feed; *m* = mole fraction of monomers in the copolymer.

Figure 4.15 is clearly shown that the mole fraction of 4-Cl-(vinyl)-PPO in copolymer is higher than mole fraction of MMA in copolymer in every ratio. Althought, some ratios have MMA higher than 4-Cl-(vinyl)-PPO. This is probably because the polymer radical of 4-Cl-(vinyl)-PPO unit at the chain end is considerably more active than the MMA units, which means that the addition of 4-Cl-(vinyl)-PPO will be more rapid than in the MMA units.

The reactivity ratios were calculated using the linear equation proposed by Fineman-Ross[16].

$$G = r_1F - r_2$$

Where G and F represented by

$$G = \frac{X(Y-1)}{Y} \quad \text{and} \quad F = \frac{X^2}{Y}$$

Where X and Y are the ratios of the mole fractions of the monomers in the feed and in the copolymer formed(Table 4.8).

Table 4.8 The F-R parameters for a 4-Cl-(vinyl)-PPO-MMA copolymer system

Sample	$X = M_1/M_2$	$Y = m_1/m_2$	$G = X(Y-1)/Y$	$F = X^2/Y$
1	0.111	2.003	0.056	0.006
2	0.429	3.500	0.306	0.053
3	1.500	4.000	1.125	0.563
4	2.300	4.997	1.839	1.059
5	4.000	6.001	3.333	2.666
6	9.000	11.008	8.182	7.358

M_1 is mole fraction of 4-Cl-(vinyl)-PPO in feed; M_2 is mole fraction of MMA in feed; m_1 is mole fraction of 4-Cl-(vinyl)-PPO in copolymer; m_2 is mole fraction of MMA in copolymer

From Table 4.8, *G* was plotted against *F* (Figure 4.15) to yield a straight line with slope r_1 and intercept r_2.

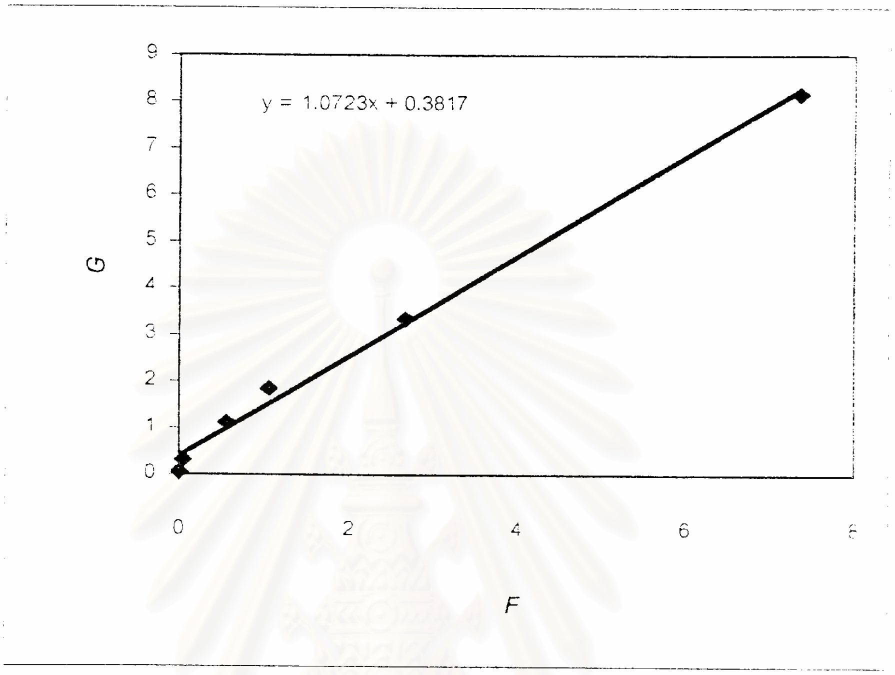

Figure 4.16 Fireman-Ross plot

r_1 is the reactivity ratio of 4-Cl-(vinyl)-PPO and r_2 is the reactivity ratio of MMA. The value of r_1 and r_2 obtained from the F-R plot are $r_1 = 1.07$ and $r_2 = 0.38$. The value of r_1 is more than 1 and that of r_2 is less than 1, and this indicates that 4-Cl-(vinyl)-PPO is more reactive than MMA. The r_1 and r_2 values suggest that the system represents a random copolymerization.

The structure molecule of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole is larger than the structure molecule of methyl methacrylate. Thus, methyl methacrylate should be more active than 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole, but in this study it indicated that 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole is more active than methyl methacrylate from *r* values.

In this case, the less reactivity of methyl methacrylate monomer is probably due to the chemical nature of the polymerizable end group. Considering the structure of 4-Cl-(vinyl)-PPO, it is clearly shown that the 4-Cl-(vinyl)-PPO molecule has lone pair electron at =N- position on oxazole ring which is electron donating group effective to delocalize on π-bond of 4-Cl-(vinyl)-PPO. This effect involves the reactivity on vinyl group of 4-Cl-(vinyl)-PPO. On the other hand, the structure of MMA contains carbonyl group(C=O) which is electron withdrawing group, involves reduced reactivity on vinyl group of MMA as shown in Figure 4.17.

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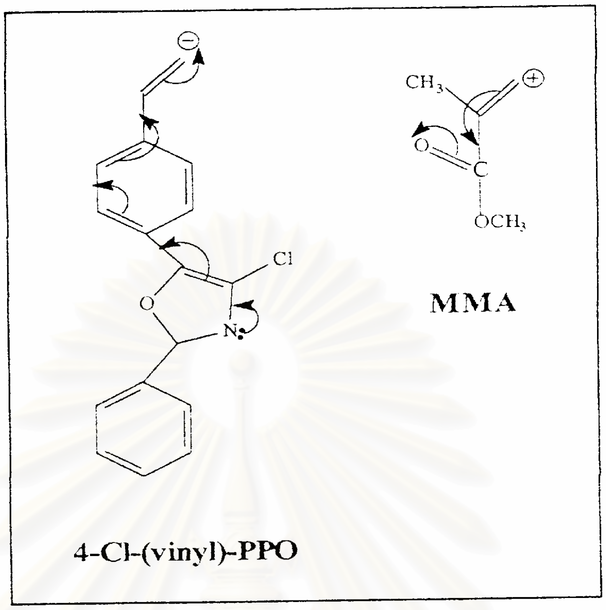

Figure 4.17 The chemical structures of 4-Cl-(vinyl)-PPO and MMA

However, the radical copolymerization may be depended on several factors, such as, the reaction medium (solvent) considering its polarity, pH, etc.

Deviations are also observed in some copolymerizations where the copolymer formed is poorly soluble in the reaction medium . Under these conditions, altered copolymer compositions are observed if one of the monomers is preferentially added by the copolymer. Thus for methyl methacrylate(M$_1$)-*N*-vinylcarbazole(M$_2$) copolymerization, r_1=1.8, r_2=0.6 in benzene but r_1=0.57, r_2=0.75 in methanol [18].The propagating polymer chains are completely soluble in benzene but are microheterogeneous in methanol.

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Some effect of viscosity on reactivity ratio has been observed. Copolymerization of styrene(M_1)-methyl methacrylate (M_2) in bulk leads to a copolymer containing less styrene than when reaction is carried out in benzene solution [19]. The gel effect in bulk polymerization decreases the mobility of styrene resulting in a decrease in r_1 and an increase in r_2.

The monomer reactivity ratio for an acidic and basic monomer shows dependence on pH since the identity of the monomer changes with pH. For example, acrylic acid(M_1)-acrylamide(M_2) copolymerization shows $r_1 = 0.90$, $r_2 = 0.25$ at pH = 2 but $r_1 = 0.30$, $r_2 = 0.95$ at pH = 9 [20-21]. A related phenomenon is the increase in the monomer reactivity ratio for ethyl-3-oxo-4-pentenoate when it copolymerizes with styrene in a nonpolar solvent compared to a polar solvent[22]. Ethyl 3-oxo-4-pentenoate exists in a keto-enol equilibrium with the concentration of enol increasing with solvent polarity. The enol has a higher reactivity compared to the keto form, and this results in a copolymer richer in ethyl-3-oxo-4 pentenoate in nonpolar solvent.

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Copolymerization involving the combination of polar (M_1) and nonpolar (M_2) monomers offen shows different behavior depending on the polarity of the reaction medium. The copolymer composition is richer in the less polar monomer in a polar (either aprotic or protic) solvent, compared to nonpolar solvent. Calculation of the monomer reactivity ratios shows a decrease in r_1 usually coupled with an increase in r_2 for copolymerization in the polar solvent relative to values in the nonpolar solvent. This behavior has been observed in a system such as styrene with acrylamide, acrylonitrile, 2-hydroxyethyl methacrylate, acrylic acid, or methacrylic acid and methacrylic acid with methyl methacrylate[23-26].

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4.4 Fluorescence Emission Analysis

The diluted 4-Cl-(vinyl)-PPO solutions of 1 mg in 100 mL of chloroform was analyzed. Typical fluorescence emission spectrum of 4-Cl-(vinyl)-PPO in chloroform is shown in Figure 4.17. The fluorescence emission spectrum of 4-Cl-(vinyl)-PPO exhibits band at 399 nm when excited at 260 nm.

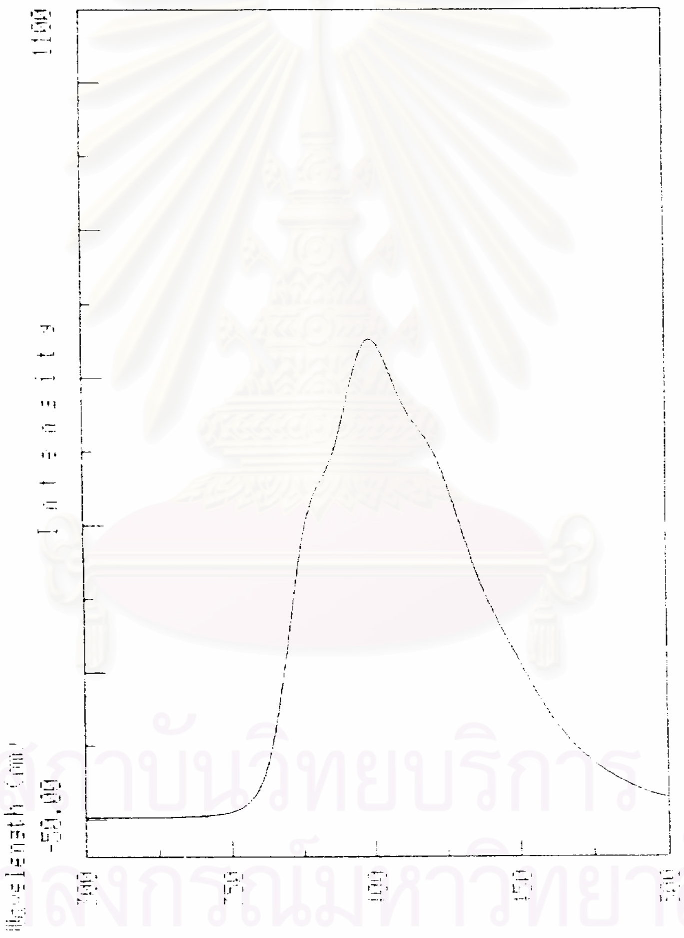

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Figure 4.18 Fluorescence emission spectra of 4-Cl-(vinyl)-PPO 1 mg in chloroform 100 mL

The copolymer of 4-Cl-(vinyl)-PPO and MMA $11x10^{-2}$ mg in 10 mL of chloroform was analyzed with excitation wavelength of 260 nm. The fluorescence emission spectrum appears at 403 nm as shown in Figure 4.18. Poly[4-Cl-(vinyl)-PPO gives fluorescence spectrum at longer wavelength than 4-Cl-(vinyl)-PPO due to the π-π interaction between carbonyl group of MMA with the phenyl ring of 4-Cl-(vinyl)-PPO. The emission wavelengths of poly[4-Cl-(vinyl)-PPO and 4-Cl-(vinyl)-PPO were little different which may involve the incorporation in copolymer of MMA less than 4-Cl-(vinyl)-PPO.

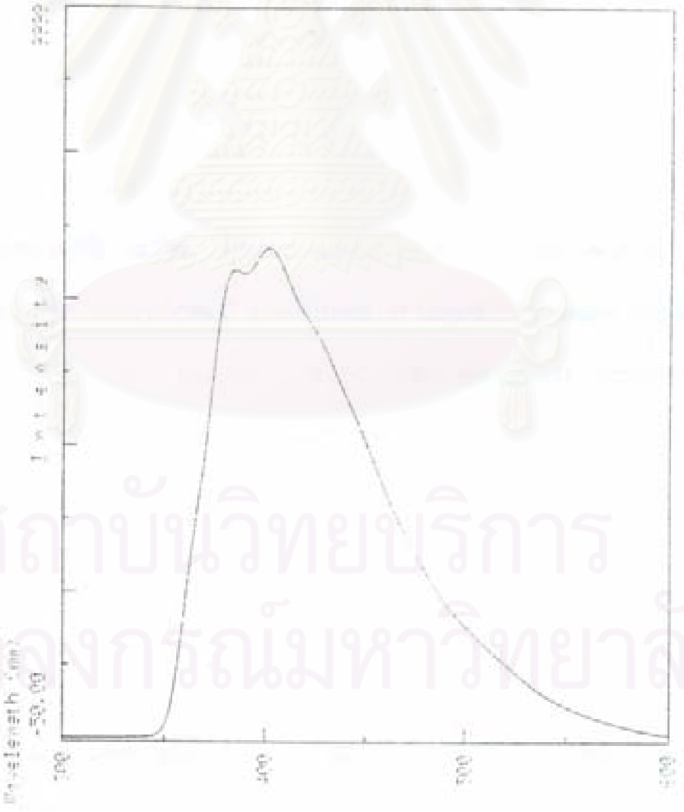

Figure 4.19 Fluorescence emission spectrum of poly[4-Cl-(vinyl)-PPO-co-MMA] $11x10^{-2}$ mg in chloroform 10 mL

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Chapter V

Conclusion

The Ternai reaction between *p*-ethylbenzaldehyde and benzoyl cyanide in a tetrahydrofuran and saturated with hydrogen chloride gave 4-chloro-2-(4′-ethylphenyl)-5-phenyloxazole. Bromination by *N*-bromosuccinimide followed by dehydrobromination with sodium *tert*-butoxide gave 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole with 51.66 % yield based on benzoyl cyanide.The spectroscopic data indicate that the required oxazoles have been obtained.

Solution polymerization of 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole with methyl methacrylate using AIBN as an initiator at 50±1 °C was carried out at six different mole ratios. The reaction time was selected at less than 10% conversion. The incorporated monomers in copolymer were calculated from gas chromatogram of the monomers feed. The monomer reactivity ratios were determined by Fineman-Ross method. The $r_{4\text{-Cl-(vinyl)PPO}}$ is greater than 1 and r_{MMA} value is less than 1, and this indicates that 4-chloro-2-(4′-vinylphenyl)-5-phenyloxazole is more reactive than methyl methacrylate. The $r_{4\text{-Cl-(vinyl)PPO}}$ and r_{MMA} values show that the system represents a random copolymerization.

The chemical structure of 4-Cl-(vinyl)-PPO influences the extent of incorporated 4-Cl-(vinyl)-PPO in copolymer because of the =N- position on oxazole ring has lone pair electron which is electron donating group by

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compairing with electron withdrawing on carbonyl group of MMA. Thus, 4-Cl-(vinyl)-PPO is more incorporated than MMA in copolymer chain.

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Appendix A

Calibration curve

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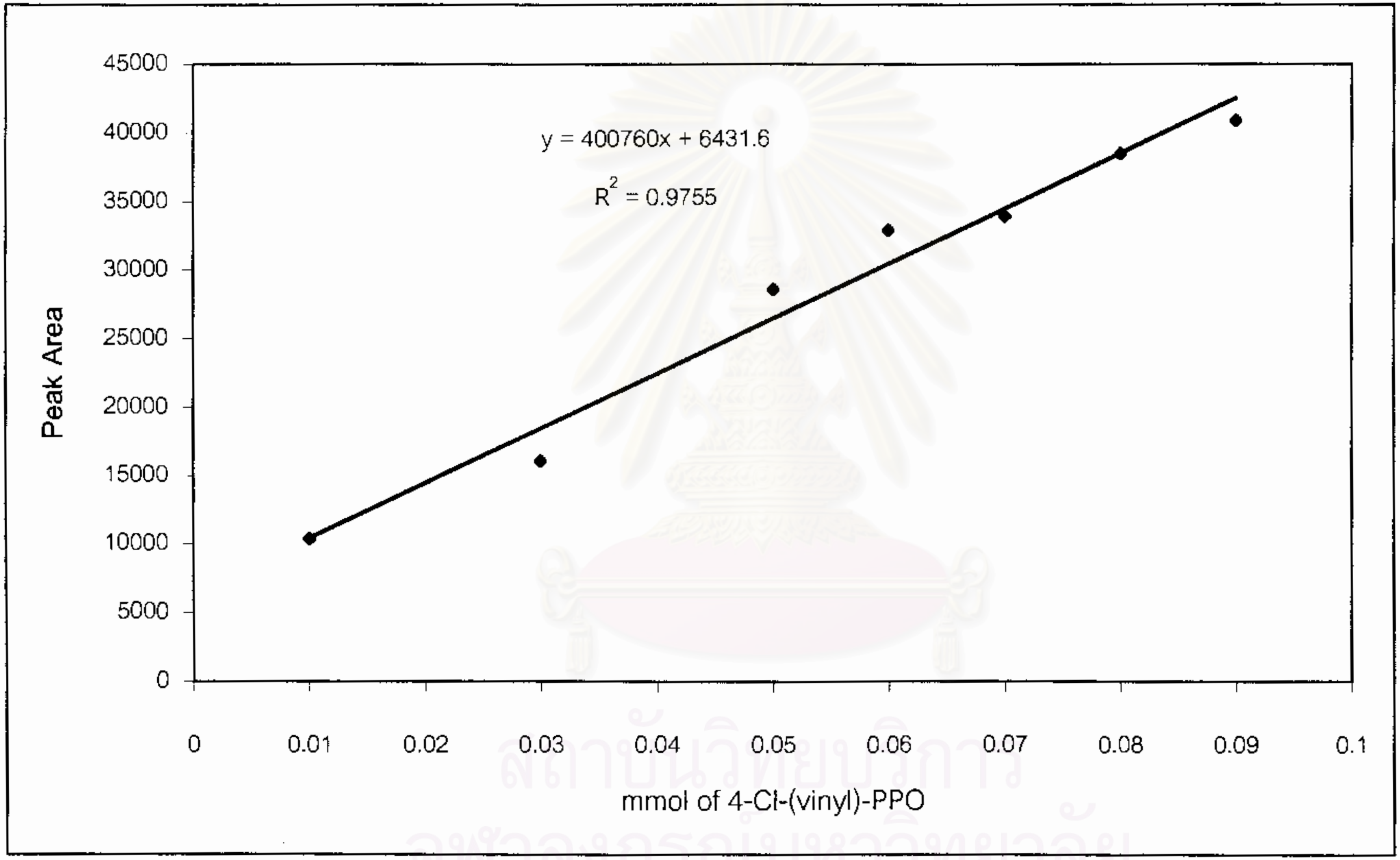

Figure A1 Calibration curve of 4-chloro-2-(4′-vinylphenyl)-5- phenyloxazole

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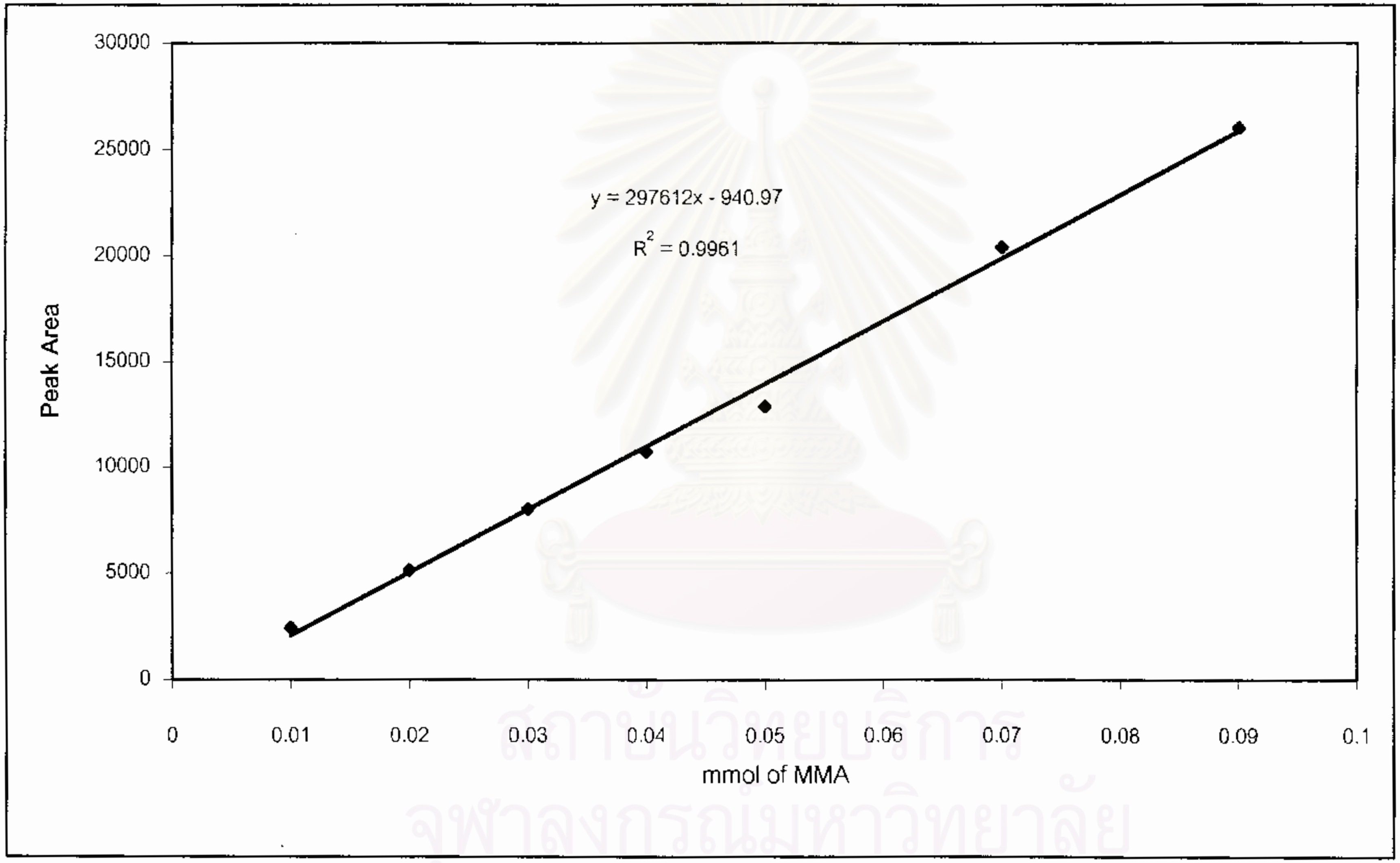

Figure A2 Calibration curve of methyl methacrylate

Appendix B

GC data

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B1: The GC data of the copolymerization at temp.= 50±1°C in different ratios and time

Table B1-1 4-Cl-(vinyl)-PPO (0.01 mmol) : MMA (0.09 mmol)

Time (min)	Peak Area					
	4-Cl-(vinyl)-PPO			MMA		
	1	2	ave.	1	2	ave.
0	11610	9136	10373	26283	25760	26021
2	10924	8456	9690	25018	26075	25546
4	8491	7610	8050	25347	25469	25408
6	7349	8462	7905	24393	25559	24976
8	7552	8022	7787	22942	26359	24600
10	7921	8688	8304	26221	22424	24322

Time (min)	% Conversion	
	4-Cl-(vinyl)-PPO	MMA
0	-	-
2	6.58	1.8
4	22.39	2.36
6	23.78	4.02
8	24.93	5.46

Table B1-2 4-Cl-(vinyl)-PPO (0.03 mmol) : MMA (0.07 mmol)

Time (min)	Peak Area					
	4-Cl-(vinyl)-PPO			MMA		
	1	2	ave.	1	2	ave.
0	15896	16230	16063	20060	20813	20436
2	16661	15245	15953	19329	17264	19296
4	14609	15317	14963	19067	19280	19173
6	14995	14859	14927	19508	18534	19021
8	14423	15041	14732	18683	17681	18182
10	15136	13799	14467	17328	18015	17671

Time (min)	% Conversion	
	4-Cl-(vinyl)-PPO	MMA
0	-	-
2	0.68	5.57
4	6.85	6.18
6	7.07	6.93
8	8.29	11.03

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Table B1-3 4-Cl-(vinyl)-PPO (0.06 mmol) : MMA (0.04 mmol)

Time (min)	Peak Area					
	4-Cl-(vinyl)-PPO			MMA		
	1	2	ave.	1	2	ave.
0	32405	33476	32940	11053	10407	10730
1	28637	29111	28874	10327	10778	10552
2	27252	27165	27208	10117	10860	10488
4	28028	26326	27177	10283	10623	10453
6	25863	26475	26169	10480	9612	10046
8	25441	24944	25192	9962	9774	9868
10	24253	24175	24214	9715	9400	9557

Time (min)	% Conversion	
	4-Cl-(vinyl)-PPO	MMA
0	-	-
1	9.22	1.65
2	13.31	2.73
4	17.50	2.58
6	20.56	6.37
8	23.52	8.03

Table B1-4 4-Cl-(vinyl)-PPO (0.07 mmol) : MMA (0.03 mmol)

Time (min)	Peak Area					
	4-Cl-(vinyl)-PPO			MMA		
	1	2	ave.	1	2	ave.
0	34804	33095	33949	8274	7774	8024
1	31949	32684	32316	7543	8253	7898
2	32433	30115	31274	7471	8024	7747
4	31814	29620	30717	7939	7417	7678
6	29983	31029	30506	7560	7315	7437
8	31089	29124	30106	7094	7799	7446
10	30158	29586	29872	7769	6504	7136

Time (min)	% Conversion	
	4-Cl-(vinyl)-PPO	MMA
0	-	-
1	4.81	1.57
2	7.88	3.45
4	9.52	4.31
6	10.14	7.31
8	11.32	7.20

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TableB1-5 4-Cl-(vinyl)-PPO (0.08 mmol) : MMA (0.02 mmol)

Time (min)	Peak Area					
	4-Cl-(vinyl)-PPO			MMA		
	1	2	ave.	1	2	ave.
0	38342	38652	38497	5013	5284	5148
1	34618	37860	36239	4868	4776	4819
2	32113	32606	32359	4078	4983	4530
4	31669	32106	31887	4853	3989	4421
6	29619	28775	29197	4482	4353	4417
8	28571	28888	28729	3824	4250	4037
10	28204	32744	30474	4362	3556	3959

Time (min)	% Conversion	
	4-Cl-(vinyl)-PPO	MMA
0	-	-
1	5.86	5.63
2	15.94	12.00
4	17.17	14.13
6	24.16	14.19
8	25.37	21.59

TableB1-6 4-Cl-(vinyl)-PPO (0.09 mmol) : MMA (0.01 mmol)

Time (min)	Peak Area					
	4-Cl-(vinyl)-PPO			MMA		
	1	2	ave.	1	2	ave.
0	40577	41196	40886	2339	2505	2422
1	38349	37549	37949	2355	2262	2308
2	35844	36627	36235	2373	2210	2291
4	34547	35570	35058	2511	2062	2286
6	34829	34882	34855	2238	2307	2273
8	35549	34145	34847	2140	2318	2229
10	35588	38141	36864	2191	2050	2120

Time (min)	% Conversion	
	4-Cl-(vinyl)-PPO	MMA
0	-	-
1	7.18	4.68
2	11.37	5.38
4	14.25	5.59
6	14.75	6.15
8	14.77	7.97

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Table B2 The GC data of copolymerization at t = 22 min and temp.= 70°C.

Ratios(mmol)		Peak Area at t = 0		Peak Area at t = 22 min	
4-Cl-(vinyl)PPO	MMA	4-Cl-(vinyl)PPO	MMA	4-Cl-(vinyl)PPO	MMA
0.05	0.45	27971	114496	11554	106344
0.10	0.40	40247	122879	14110	100984
0.15	0.35	48257	116624	17422	83847
0.20	0.30	53581	94860	18131	74120
0.25	0.25	54171	61446	22882	54561
0.30	0.20	61935	53467	25710	41837
0.35	0.15	66206	38534	30665	34516
0.45	0.05	75330	13052	37924	11349

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Ratios (m.mol)		% Conversion	
4-Cl-(vinyl)PPO	MMA	4-Cl-(vinyl)PPO	MMA
0.05	0.45	58.69	7.12
0.10	0.40	64.94	17.82
0.15	0.35	63.89	28.10
0.20	0.30	66.16	21.86
0.25	0.25	57.76	11.20
0.30	0.20	58.49	21.75
0.35	0.15	53.68	10.43
0.45	0.05	49.66	13.05

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Table B3 The GC data of copolymerization at 4-Cl-(vinyl)PPO(0.05 mmol) : MMA (0.45 mmol) in various times.

Time (min)	Peak Area					
	4-Cl-(vinyl)PPO			MMA		
	1	2	ave.	1	2	ave.
0	30968	-	30968	148934	-	148934
2	25377	19131	22254	115948	131115	123531
5	15245	19321	17283	111373	123271	117322
7	17439	18581	18010	110441	120806	115623
10	13590	18402	15996	113160	117997	115578
15	13038	17018	15028	113143	107654	110398

Time (min)	% Conversion	
	4-Cl-(vinyl)PPO	MMA
0	-	-
2	28.14	17.06
5	44.19	21.23
7	41.84	22.37
10	48.35	22.40
15	51.47	25.88

Table B4 The GC data of copolymerization at 4-Cl-(vinyl)-PPO (0.05mmol) : MMA (0.05mmol) in various times.

Time (min)	Peak Area					
	4-Cl-(vinyl)-PPO			MMA		
	1	2	ave.	1	2	ave.
0	30405	36403	33404	15242	15006	15124
1	28067	36364	32215	14468	15665	15066
2	33541	31332	32436	14313	14903	14858
5	29387	27484	28435	14340	12922	13631
7	27742	27010	27376	12676	13245	12960
10	27015	24285	25650	12857	13045	12951

Time (min)	% Conversion	
	4-Cl-(vinyl)-PPO	MMA
0	-	-
1	3.56	0.38
2	2.89	1.76
5	14.87	9.87
7	18.05	14.31
10	23.21	14.36

Vita

Miss Dhidaratana Hirunviriya was born on March 25, 1974 in Yala. She graduated with a Bachelor degree of Science (Polymer Science) from Prince of Songkhla University in 1995. Since then she was accepted as graduate student in the program of Petrochemistry and Polymer Science, Chulalongkorn University. She received a Master's Degree of Science in 2000.

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