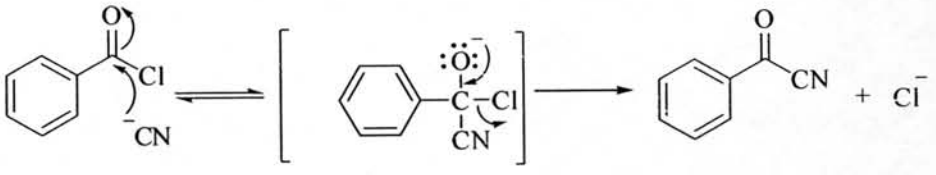
CHAPTER IV

RESULTS AND DISCUSSION

Part A : Synthesis

4.1 Synthesis of benzoyl cyanide [2]

Benzoyl cyanide was synthesized from the corresponding benzoyl chloride **[1]** and cuprous cyanide. Benzoyl chloride reacted with a cyanide ion through the addition-elimination mechanism of nucleophilic acyl substitution as shown in **Scheme 4.1**. Due to the high reactivity of benzoyl chloride, anhydrous condition is required. Thus cuprous cyanide must be dried before use.



[1] **[2]**

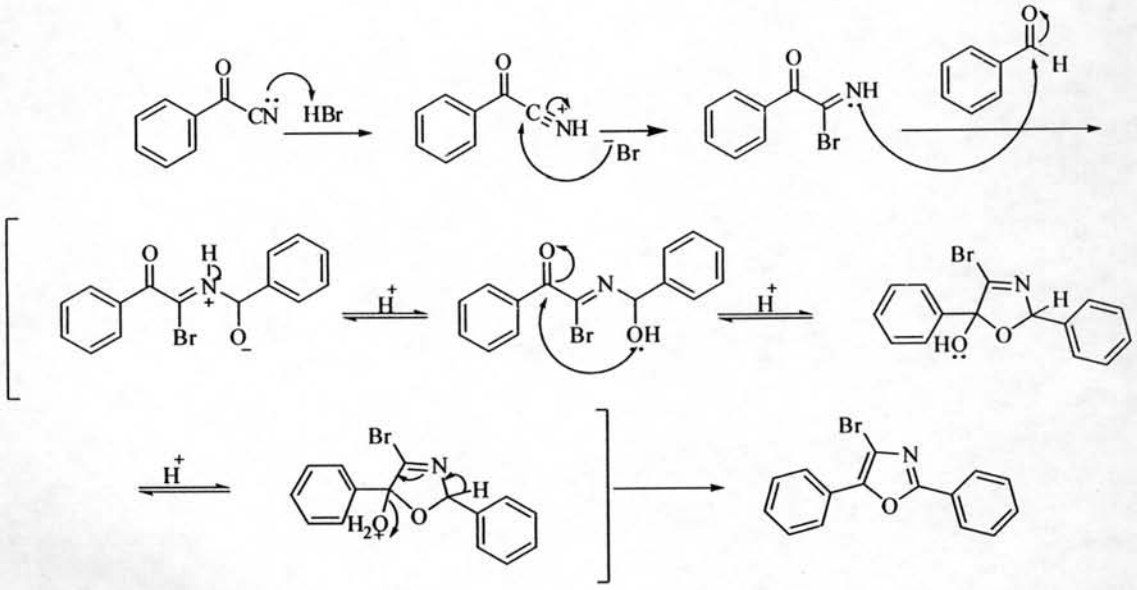
Scheme 4.1: The addition-elimination mechanism of nucleophilic acyl substitution.

Benzoyl cyanide **[2]** was colorless liquid with 65% yield. FT-IR data shows the red shift of the carbonyl absorption from 1780 cm^{-1} of benzoyl chloride to about 1685 cm^{-1} of benzoyl cyanide. While the disappearance of the C-Cl at 1175 cm^{-1} in concomitant with the appearance of cyanide at 2222 cm^{-1} was observed. The ^{1}H NMR spectrum of benzoyl cyanide in chloroform-*d* exhibited the chemical shifts of aromatic protons as a 1H triplet (J = 6 Hz) at δ 7.56 ppm, a 2H triplet (J = 2 Hz) at δ 7.77 ppm and a 2H doublet (J = 2 Hz) at δ 8.10 ppm. with correct integration ratios. It was clearly revealed by the appearance of the ^{13}C signal at 112.8 ppm, which is the characteristic signal for a nitrile carbon. According to these data, it could be concluded that the product was benzoyl cyanide.

4.2 Synthesis of 4-bromo-2,5-diphenyloxazole [4]

After the benzoyl cyanide **[2]** was obtained, the next step was to design and synthesize 4-bromo-2,5-diphenyloxazole **[4]**. The compound **[4]** was obtained from the cyclization reaction of benzoyl cyanide with benzaldehyde **[3]** in diethyl ether saturated with hydrogen chloride in one-step. The reaction yield was 65%. A possible mechanism for this cyclization reaction is shown in **Scheme 4.2**.

The method of Ternai [40] has been prepared using modified Fischer synthesis from the one step reaction but they did not supply very much detail. Therefore, in this study, the mechanism of the 4-bromo-oxazole formation is proposed. First, the addition of HCl onto the cyano group gave acylimidoyl chloride. Then, acylimidoyl chloride promptly attacked the aldehyde carbonyl carbon and reaction proceeded by the cyclization by losing water.



Scheme 4.2: Mechanism of oxazole formation.

The FT-IR spectrum of this compound shows an absorption peak at 1580 cm^{-1}, which was assigned to the vibration arising from oxazole ring system. The ^{1}H NMR spectrum in chloroform-d exhibits the characteristic of aromatic proton indicated a 2H multiplet at δ 8.11-8.08 ppm corresponding to the aromatic protons at positions 2″

and 6″ of benzene ring, a 2H doublet (J = 7 Hz) at δ 7.95 ppm corresponding to the aromatic protons at positions 2′ and 6′ of benzene ring, a 5H multiplet at δ 7.51-7.48 belonging to the aromatic protons at positions 3″, 4″, 5″, 3′ and 5′ of benzene ring, and a 1H triplet (J = 7.5 Hz) at δ 7.39 ppm belonging to the aromatic proton at position 4′ of benzene ring (Figure 4.1).

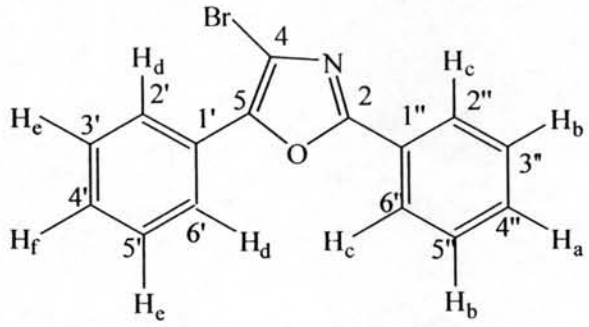


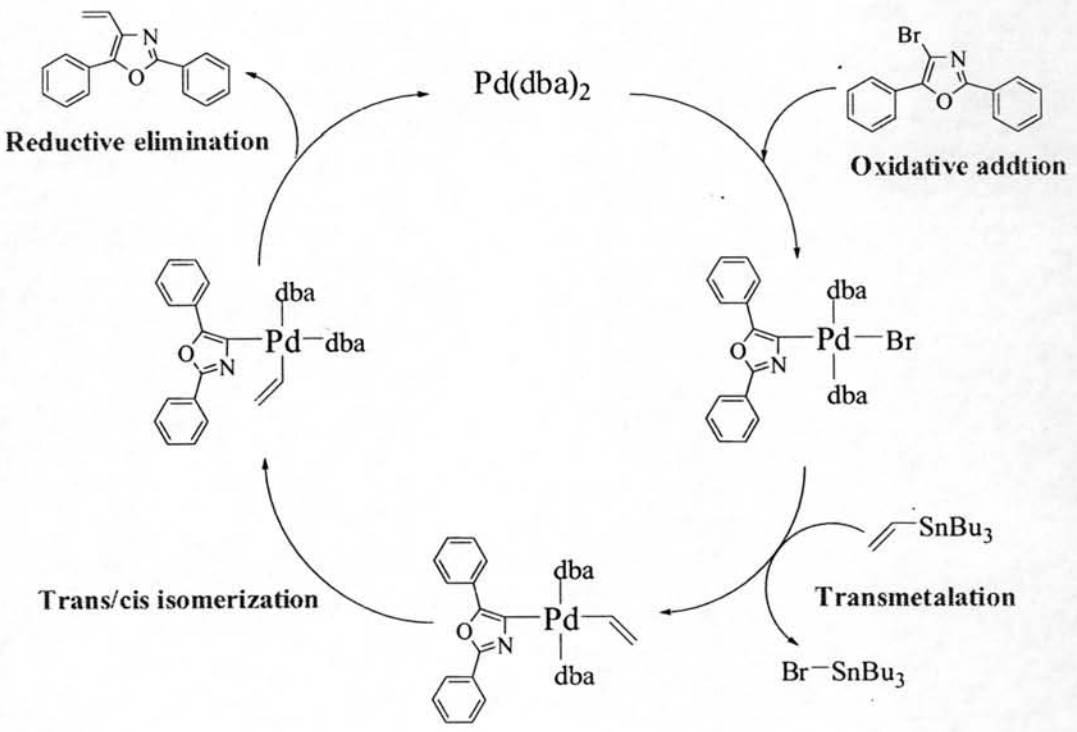
Figure 4.1 Chemical structure of 4-Bromo-2,5-diphenyloxazole with atomic numbering.

The ^{13}C NMR spectrum of 4-bromo-2,5-diphenyloxazole (Figure B2) could be achieved by comparing with that of PPO. Firstly, the carbons of the oxazole ring in PPO could be assigned by using the phenyl group substitute effect on the C-2 and C-5 of oxazole itself. The calculated chemical shift positions of C-2 and C-5 are 158.9 and 143.9 ppm, respectively. According to these data, it could be concluded that the product was 4-bromo-2,5-diphenyloxazole.

4.3 Synthesis of 2,5-diphenyl-4-vinyloxazole [5]

After the 4-bromo-2,5-diphenyloxazole **[4]** was obtained, the next step was to design and synthesize 2,5-diphenyl-4-vinyloxazole **[5]** functionalized with polymerizable groups. The design of the functionalized monomers had to fulfill a number of important criteria. The designed monomer had to function effectively as a scintillant molecule and be readily polymerized. To ensure that the designed monomers were able to scintillate, they were based upon PPO, which is a well-known scintillating molecule. It was expected that the molecule containing this oxazole moiety should retain the ability to scintillate.

2,5-Diphenyl-4-vinyloxazole **[5]** was prepared from coupling reaction of 4-bromo-2,5-diphenyloxazole**[4]** with tributyl(vinyl)tin in 1-methyl-2-pyrrolidinone. The reaction yield was 50%. A possible mechanism for this Stille coupling reaction is shown in **Scheme 4.3**.



Scheme 4.3: Mechanism of Stille coupling reaction.

The method of stille coupling reaction method has been prepared from the one step reaction. Therefore, in this study, the mechanism of the 2,5-diphenyl-4-vinyloxazole formation is proposed. First, the oxidative addition of 4-bromo-2,5-diphenyloxazole into tris(dibenzylidineacetone)dipalladium(0) gave organopalladium bromide. Then, organopalladium bromide was treated with tributyl(vinyl)tin by the transmetalation. Next, organopalladium was converted form from trans to cis by trans/cis isomerization. Finally, 2,5-diphenyl-4-vinyloxazole was pushed by the reductive elimination.

The FT-IR spectrum of 2,5-diphenyl-4-vinyloxazole shows an absorption peak at 1637 cm^{-1}, which was assigned to the vibration arising from C=C stretching. The ^{1}H NMR spectrum in chloroform-d exhibits the characteristic doulet at 6.79 ppm coupling with doulet at 6.28 ppm and doulet at 5.47 ppm.

4.4 Synthesis of 2,5-diphenyl-4-vinyloxazole-*co*-methyl methacrylate polymers [6]

2,5-Diphenyl-4-vinyloxazole monomer was copolymerized with MMA under radical condition by suspension polymerization method at 65°C for 10 hours. After product purification, the polymerization was monitored by ^{1}H-NMR spectroscopy, by checking the disappearance in the spectra of the vinylidenic proton of monomeric oxazole gave chemical shifts in the range of 5.47-6.79 ppm as shown in **Figure 4.2**.

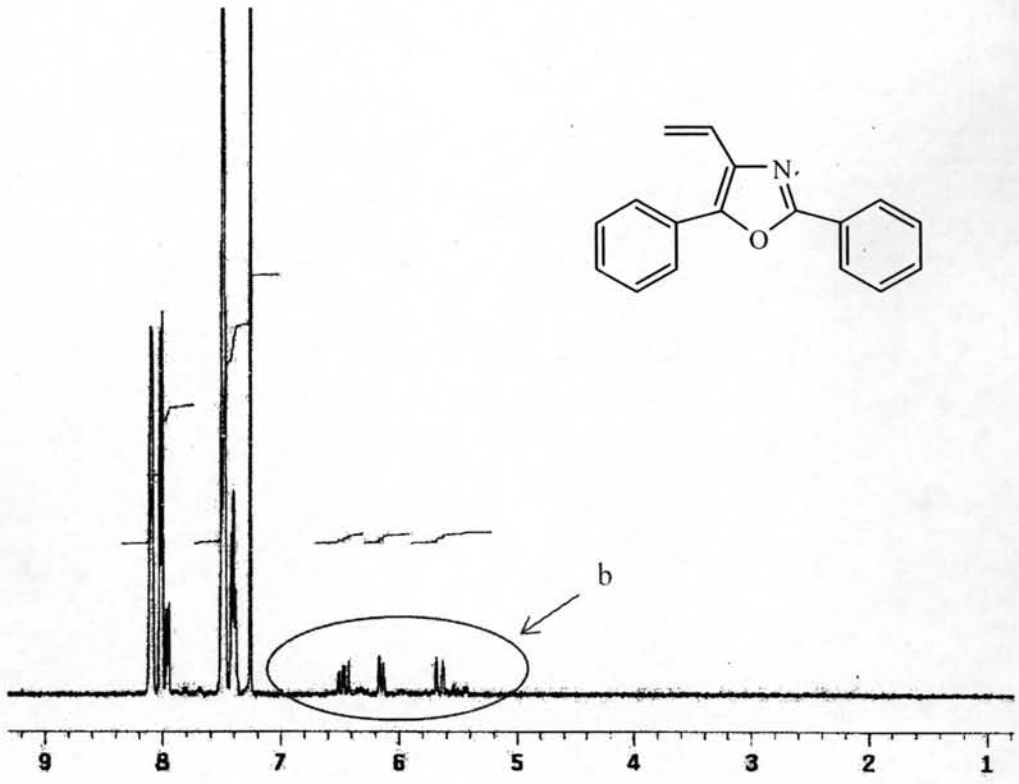


Figure 4.2: ^{1}H-NMR spectrum of 2,5-diphenyl-4-vinyloxazole **[5]**.

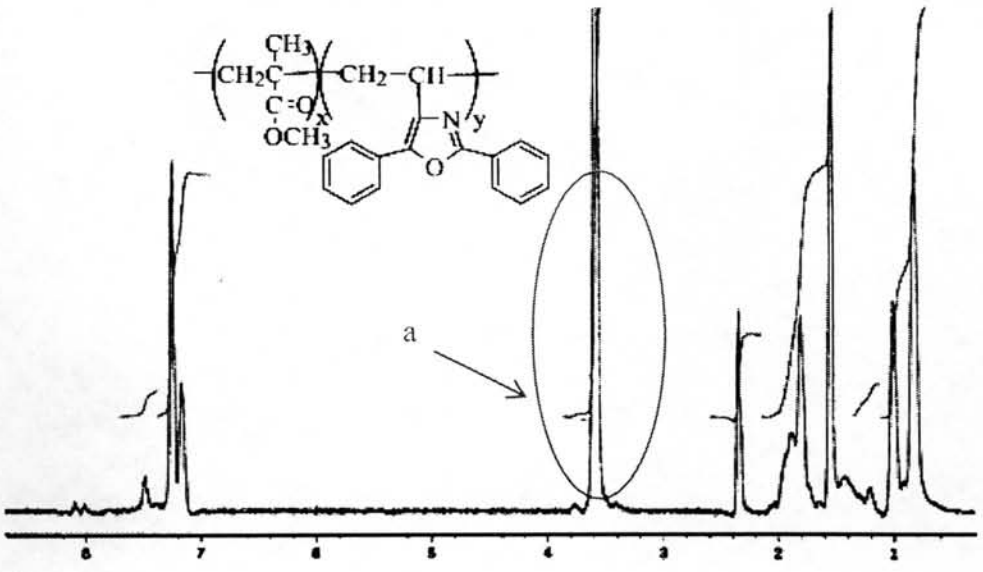


Figure 4.3: ^{1}H-NMR spectrum of **2**,5-diphenyl-4-vinyloxazole-*co*-methyl methacrylate polymers **[6].**

For the polymer, ^{1}H NMR show no evidence of unreacted vinyl group, indicating that separation of the monomer reactants from the polymer product was essentially complete.

The molar composition of copolymers can be calculated by ^{1}H-NMR spectroscopy comparing the integration of the singlet signal due to the methyl ester group of MMA, located at 3.63 ppm ("a" from Figure 4.3), and the vinyl proton of 2,5-diphenyl-4-vinyloxazole at in the range of 5.47-6.79 ppm ("b" from Figure 4.2).

4.5 Synthesis of 2,5-diphenyl-4-vinyloxazole-co-styrene polymers [7]

2,5-Diphenyl-4-vinyloxazole monomer was copolymerized with styrene under radical condition in dry toluene at 65°C for 48 hours. After product purification, the polymerization was monitored by ^{1}H-NMR spectroscopy, by checking the disappearance in the spectra of the vinylidenic proton of monomeric oxazole gave chemical shifts in the range of 5.47-6.79 ppm as shown in **Figure 4.2**.

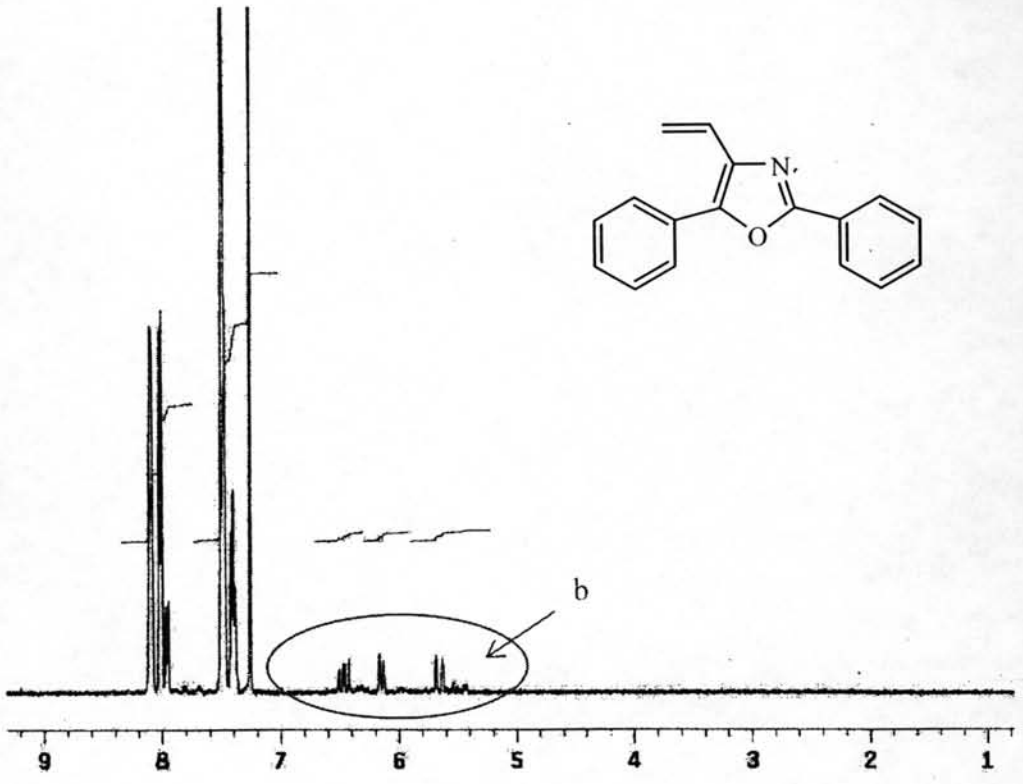


Figure 4.2: ^{1}H-NMR spectrum of 2,5-diphenyl-4-vinyloxazole **[5]**.

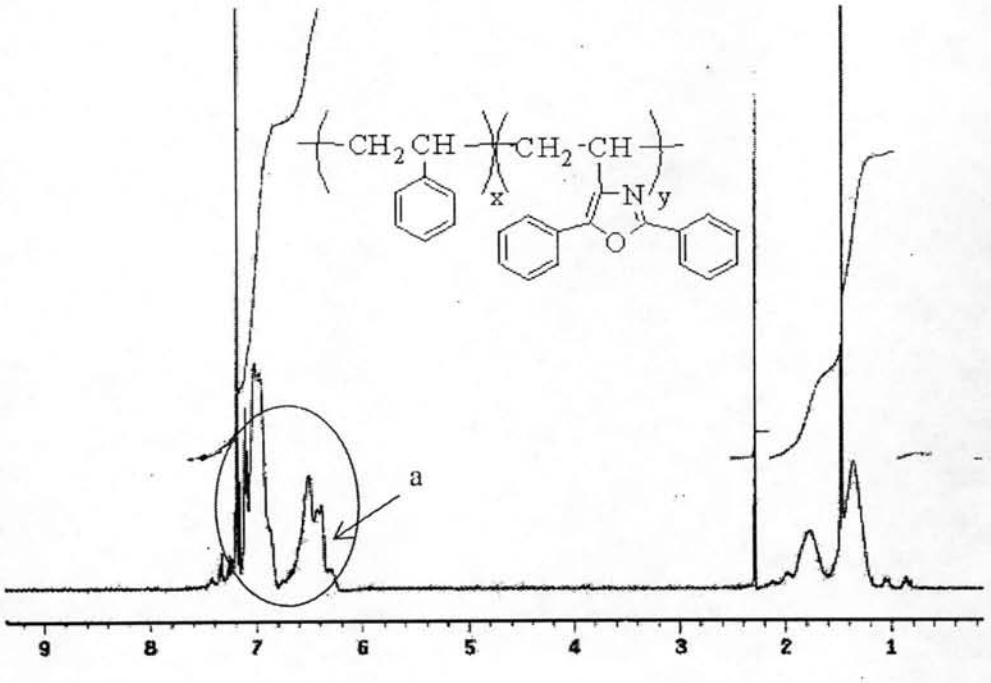


Figure 4.4: ^{1}H-NMR spectrum of 2,5-diphenyl-4-vinyloxazole-*co*-styrene polymers [7].

For the polymer, ^{1}H NMR show no evidence of unreacted vinyl group, indicating that separation of the monomer reactants from the polymer product was essentially complete.

The molar composition of copolymers can be calculated by ^{1}H-NMR spectroscopy comparing the integration of the multiplet signal due to the benzene group of styrene, located at 6.26-6.68 ppm ("a" from Figure 4.4), and the vinyl proton of 2,5-diphenyl-4-vinyloxazole at in the range of 5.47-6.79 ppm ("b" from Figure 4.2).

4.6 Determination of molecular weight

The molecular weights and polydispersities of polymers at different were shown in **Table 4.1**.

Table 4.1: Polymerization results of polymers.

Polymer	*Mn*	*Mw*	PDI
[6]	60,274	85,727	1.42
[7]	13,111	19,226	1.47

The molecular weights of these polymers were determined by GPC using monodisperse polystyrenes as the standard. As depicted in **Table 4.1**, the weight-average molecular weights (*M*w) of MMA copolymer is 85,727 and styrene copolymer is 19,226 with polydispersity indices (*M*w/*M*n) in the range 1.42-1.47

4.7 Determination of thermal properties

The thermal stability of all polymeric derivatives, as determined by TGA, was relatively high. Most of polymers were not as thermally stable as PMMA (250°C) and PS (400°C). The temperatures at which they underwent 5% weight losses (*Td*) when subjected to TGA under N_2 with a heating rate of 10°C/min ranged of MMA copolymer from 169°C and styrene copolymer from 365°C

Table 4.2: Thermal properties of polymers.

Polymer	*Tg* (°C)	*Td* (°C)
[6]	104	169
[7]	96	365

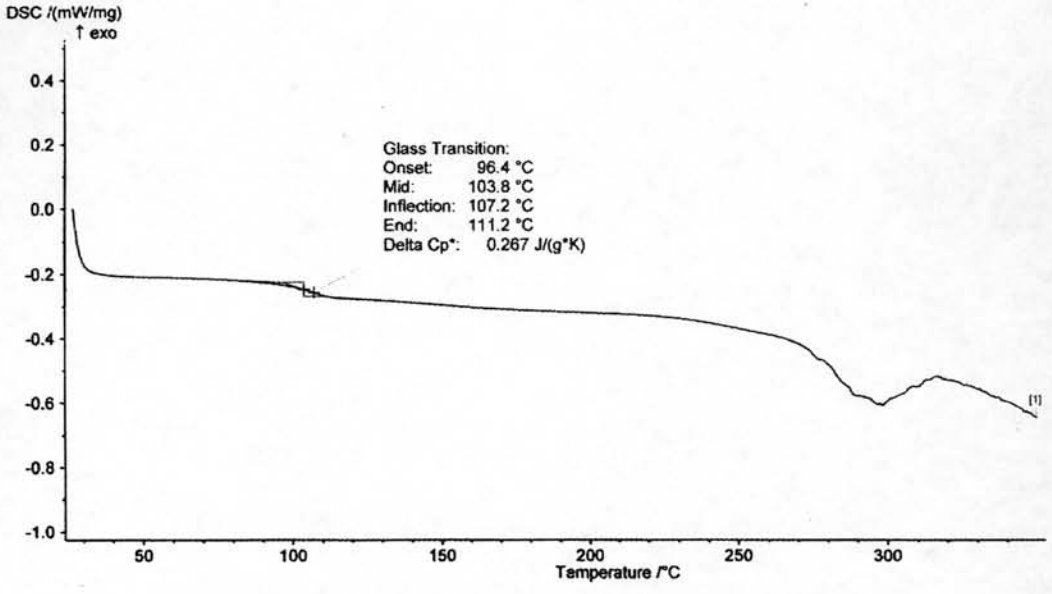


Figure 4.5: DSC Thermogram of MMA copolymer.

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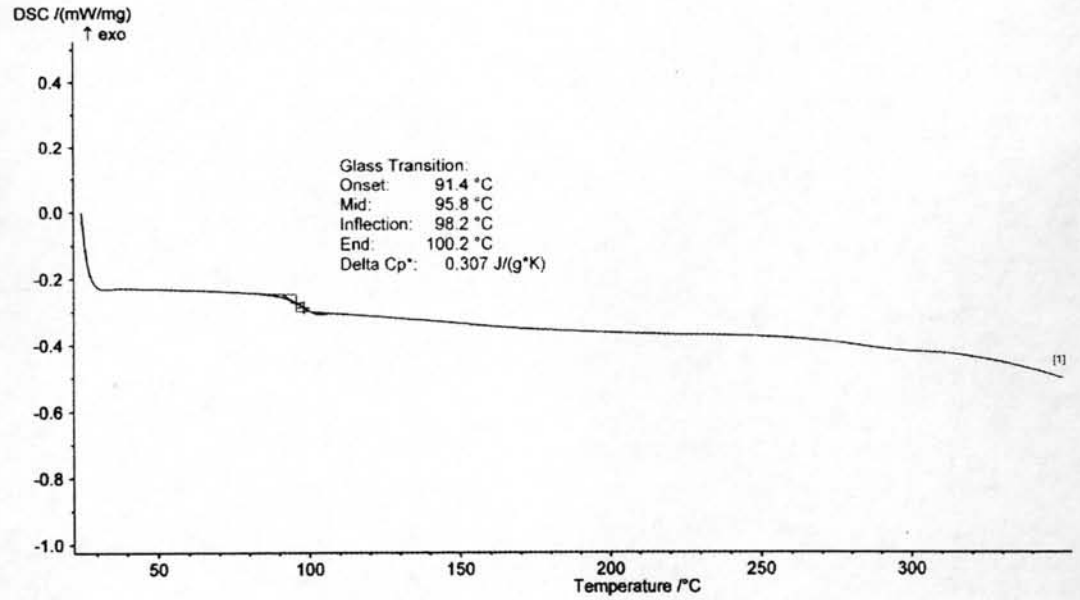

Figure 4.6: DSC Thermogram of styrene copolymer.

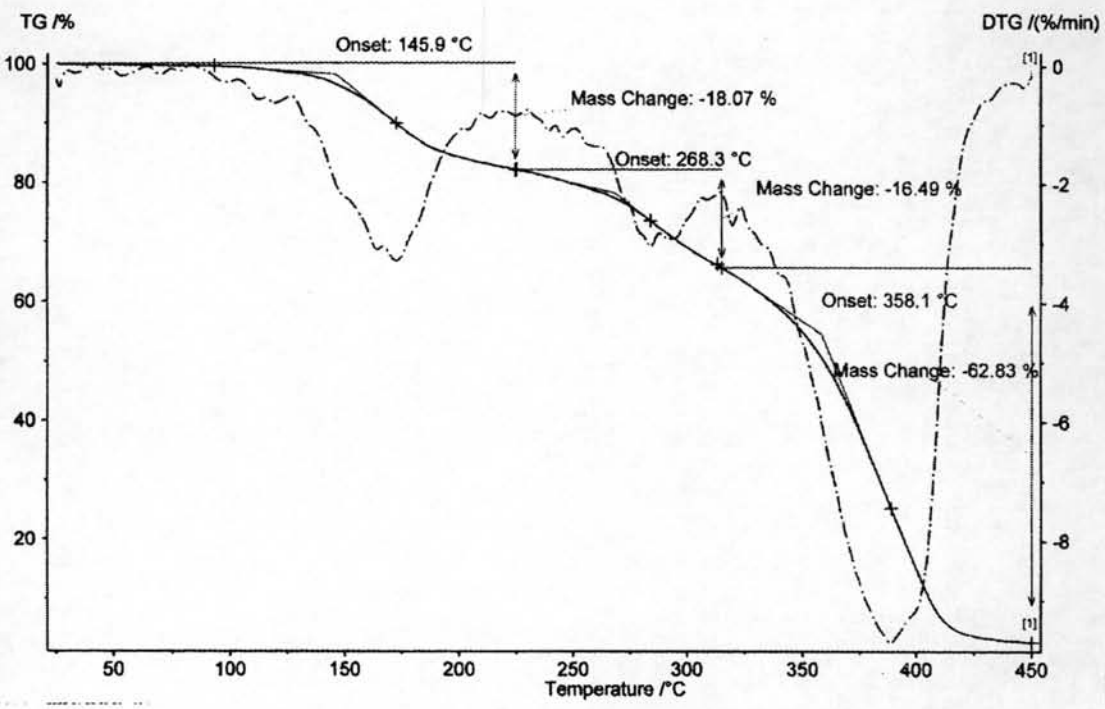

Figure 4.7: Thermogravimetric curve of MMA copolymer.

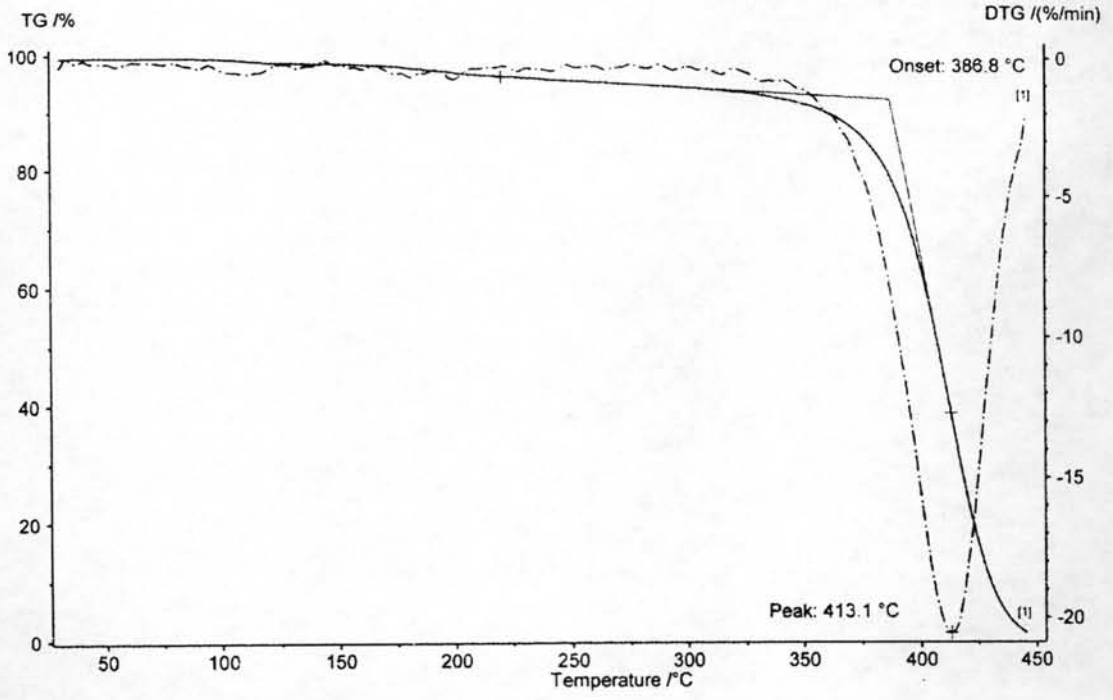

Figure 4.8: Thermogravimetric curve of styrene copolymer.

4.8 Polymer solubility

The polymers containing 2,5-diphenyloxazole as a pendent chain show good solubility in a number of common organic solvents. **Table 4.3** summarizes the results of qualitative solubility tests.

Table 4.3: Solubility of polymers.

Polymer	THF	Toluene	$CHCl_3$	NMP	DMPU
[6]	+	+	+	+	+
[7]	+	+	+	+	+

(+) Soluble

The good solubility of these oxazole-containing polymers is in marked contrast to the behavior of other analogue polymers with five-membered heteroaromatic rings. For example, polymers with thiazole groups are soluble in 1-methyl-2-pyrrolidinone (NMP) at room temperature but insoluble in Tetrahydrofuran (THF), even on heating. The thiazole rings result in more extended geometry of the repeating unit. As a result, the backbones of the thiazole polymers are less flexible than those of oxazole polymers.

Part B : Optical properties

4.9 Optical properties of 2,5-diphenyl-4-vinyloxazole [5]

2,5-Diphenyloxazole, a parent molecule, normally shows a strong maximum absorption at 305 nm, a maximum emission at 376 nm and fluorescent quantum yield of 0.18. The characteristic absorption spectrum of 2,5-diphenyloxazole consists of two absorption bands depending upon the nature of the phenyl substituents at 315-360 nm ($\varepsilon_{max} > 10^3$), and 260-299 nm ($\varepsilon_{max} < 10^3$), respectively. The low-energy absorption is attributed to extended conjugation via the resonance structure while the high-energy absorption is due to π-π^* transition [31]

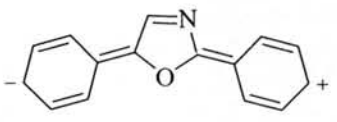

Figure 4.9: Extended conjugation via the resonance structure of 2,5-diphenyloxazole.

The effect of functional substituents on the spectral characteristics and luminescence intensity of 2,5-diphenyl-4-vinyloxazole **[5]** has been studied according to the Lambert Beer's law and compared to the 2,5-diphenyloxazole spectral data. The absorption and emission maxima, extrinction coefficient and fluorescence quantum yields are given in **Table 4.4**.

Table 4.4: Optical properties of 2,5-diphenyl-4-vinyloxazole **[5]**.

Compound	λ_{abs} [(a)] (nm)	Log ε	λ_{em} [(a)] (nm)	ϕ_f [(b)]
PPO	305	4.49	361	0.18
[5]	312	4.58	375	0.10

[(a)] Solvent tetrahydrofuran, $c = 1x10^{-5}$ mol/L for absorption measurements, $c = 1x10^{-7}$ mol/L for emission measurements. - [(b)] External standard was anthracene.

4.9.1 Absorption spectra

The absorption spectra of 2,5-diphenyl-4-vinyloxazole **[5]** was measured in THF at the concentration of $1x10^{-5}$ M.

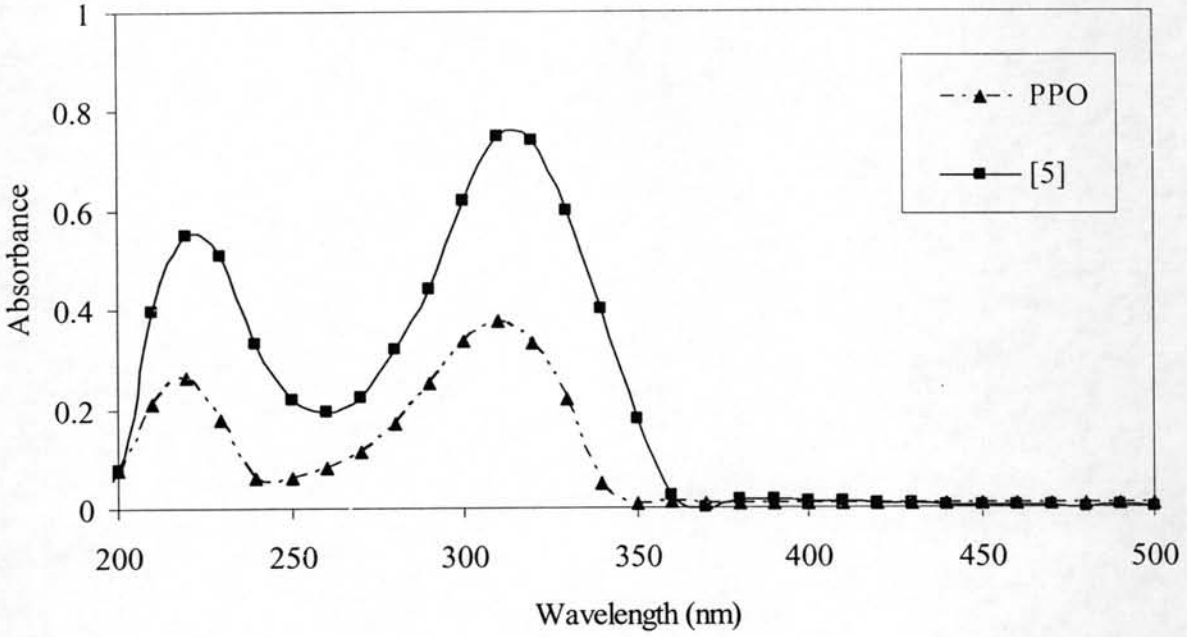

Figure 4.10: Absorption spectra of compound **[5]** and PPO in $1x10^{-5}$M.

Compared to parent 2,5-diphenyloxazole (PPO), the absorption maximum of 2,5-diphenyl-4-vinyloxazole showed a distinct bathochromic shift ($\Delta\lambda_{abs}$= +7 nm). The nearly unaltered shape of the absorption bands implied that the absorption peak is caused by same contribution of vibronic states. It is well known that substituents can affect the spectral data through conjugated π-system effect.

4.9.2 Emission spectra

The emission spectra of 2,5-diphenyl-4-vinyloxazole **[5]** was measured in THF at the concentration of $1x10^{-7}$ M. Emission spectra show features similar to those of the absorption spectra. Introduction of vinyl substituents shift the emission maxima to longer wavelengths.

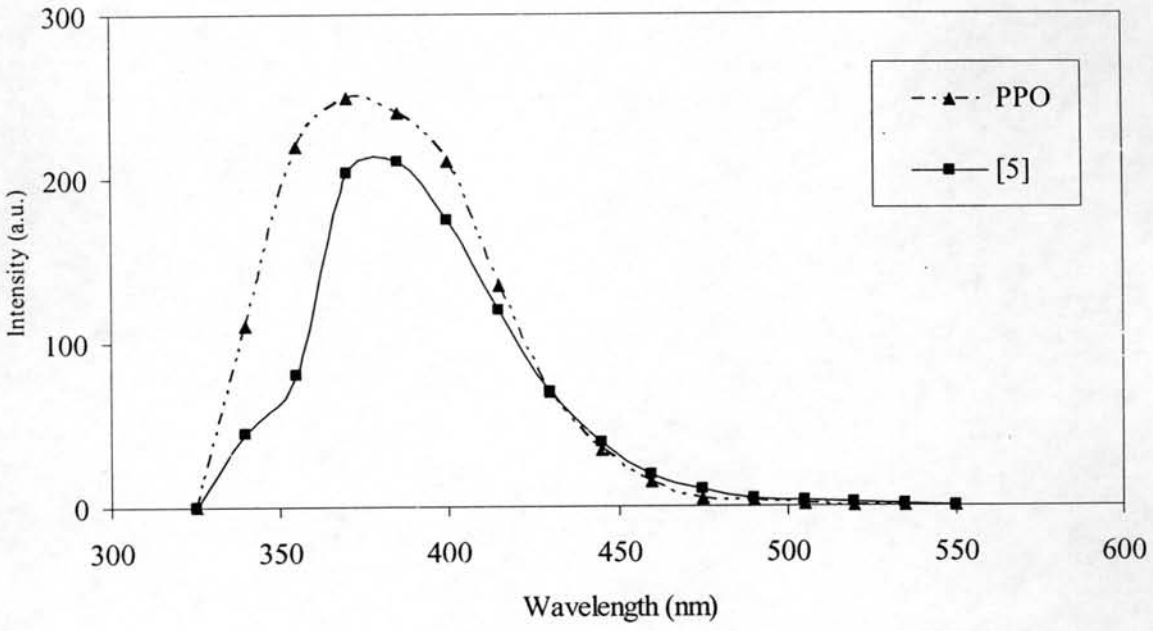

Figure 4.11: Emission spectra of compounds **[5]** and PPO at same concentration.

The differences in positions of long-wavelength absorption band observed for the emission spectra of 2,5-diphenyl-4-vinyloxazole [5] and PPO as shown in **Figure 4.11.** The effect of extending the conjugated π-system is seen in 2,5-diphenyl-4-vinyloxazole ($\Delta\lambda_{abs}$= +14 nm).

4.9.3 Quantum yield

2,5-Diphenyl-4-vinyloxazole investigated in this study show a bright fluorescence in solution, which was quantified in THF at ambient temperature by the optical diluted solution method [20]. Anthracene in ethanol was used as standard. Systematic errors of ± 5% should be taken into account. The values obtained for 2,5-diphenyl-4-vinyloxazole **[5]** (ϕ_f = 0.1) is lower than PPO. A decrease in fluorescence intensity was found especially in the systems in which substituent was incorporated in the system as a consequence of color quenching effects.

4.10 Optical properties of polymers

The absorption and fluorescence spectra of the polymers were studied and compared to the data previously obtained for monomers. The absorption and emission maxima and fluorescence quantum yields are given in **Table 4.5.**

Table 4.5: Optical properties of polymers.

Polymer	$\lambda_{abs}^{(a)}$ (nm)	Log ε	$\lambda_{em}^{(a)}$ (nm)	$\phi_f^{(b)}$
[6]	312	5.06	375	0.13
[7]	325	5.33	401	0.16

[(a)] Solvent tetrahydrofuran, $c = 1x10^{-5}$ mol/L for absorption measurements, $c = 1x10^{-7}$ mol/L for emission measurements. - [(b)] External standard was anthracene.

4.10.1 Absorption spectra

The absorption spectra of MMA copolymer and styrene copolymer are shown in **Figure 4.12.** The broader absorption spectra were obtained the non-coplanarity and rotational freedom of individual rings.

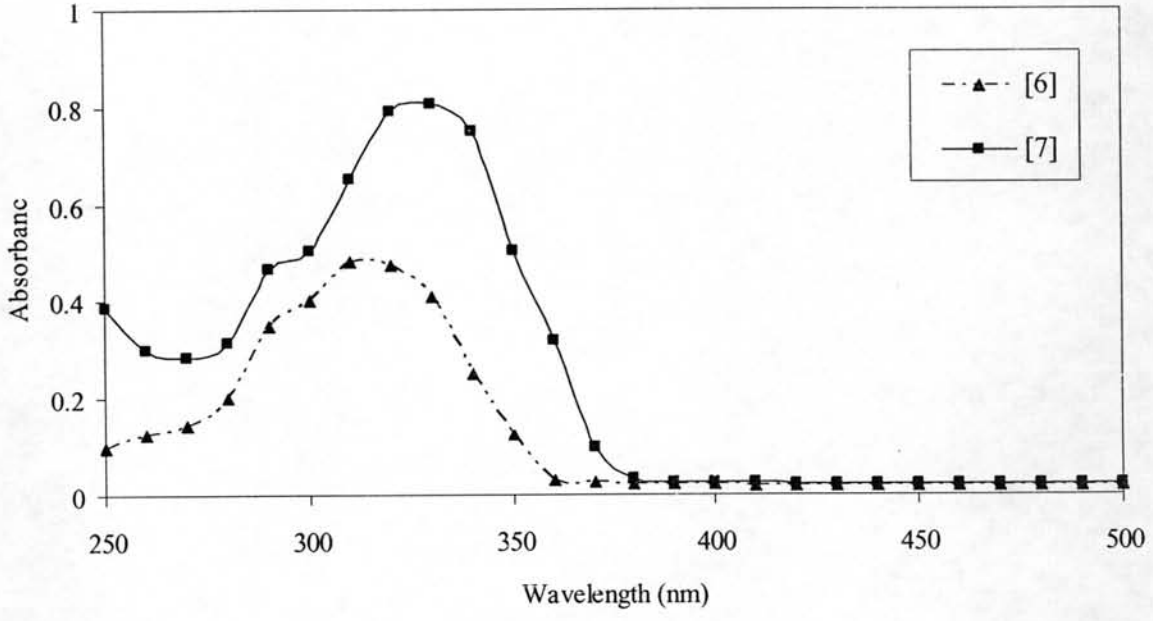

Figure 4.12: Absorption spectra of **[6]** and **[7]** at $1x10^{-5}$M.

Compared styrene copolymer and methyl methacrylate copolymer, the maximum absorption band of styrene copolymer shifts bathochromically ($\Delta\lambda_{abs}$= +13 nm).The nearly unaltered shape of the absorption bands of methyl methacrylate and styrene copolymers suggests that the absorption peak are caused by same contribution of vibronic states of 2,5-diphenyloxazole moiety.

4.10.2 Emission spectra

The emission spectra of MMA copolymer and styrene copolymer containing 2,5-diphenyloxazole moiety as a pendent chain were measured in THF.

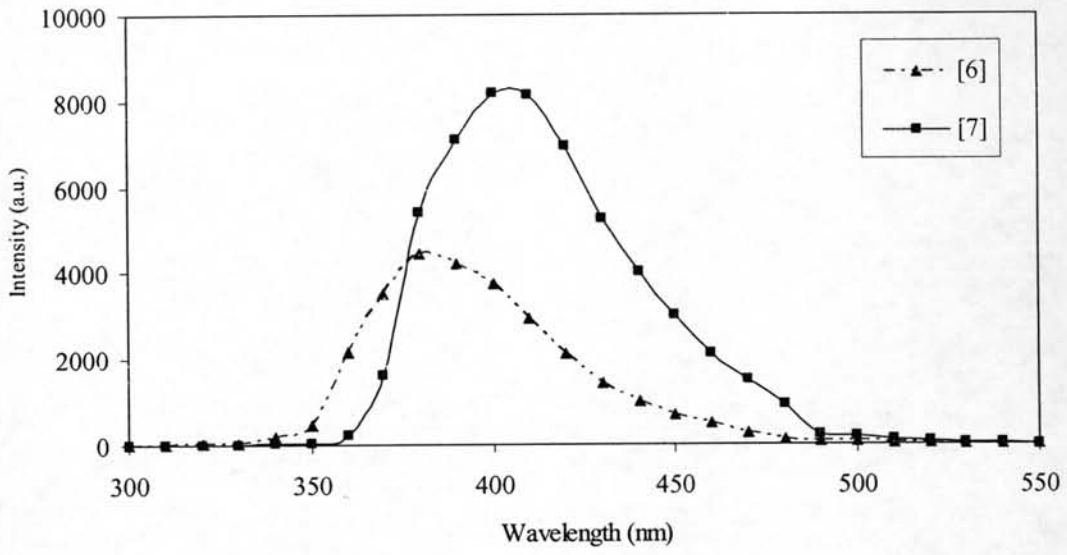

Figure 4.13: Emission spectra of **[6]** and **[7]** at $1x10^{-7}$M.

The emission spectra of methyl methacrylate and styrene copolymers containing 2,5-diphenyloxazole moiety in the polymer backbone studied in THF are shown in **Figure 4.13**. Interestingly, the broader emission spectra were obtained. It should be noted that the styrene copolymer **[7]** gave the highest fluorescence intensity.

4.10.3 Quantum yield

The highest fluorescence quantum yield is observed for **[7]**, (ϕ_f = 0.16).The 5 wt.% feed amount of 2,5-diphenyl-4-vinyloxazole with styrene monomer gave a higher fluorescent quantum yield than the 5 wt.% feed amount of 2,5-diphenyl-4-vinyloxazole with methyl methacrylate monomer.