

CHAPTER IV

STRAIN SENSITIVE PHOTONIC NATURAL RUBBER

4.1 Abstract

Photoluminescent polymers such as poly(p-phenylene vinylene) (PPV) and oligo(phenylene vinylene) (OPV) show good optical response and consequently can serve as active materials in sensor devices. Our objectives are to prepare, characterize, and develop a material for a deformation sensor. This sensor combines the properties of photoluminescent polymers, which emit light when excited by photons, and the elastic properties of natural rubber. Natural rubber, grafted with small amounts (0.5-4 wt%) of either PPV or OPV, was prepared by free radical polymerization using a classic initiator, AIBN. The results of NMR led to the calculation for the mole ratio of dye grafted natural rubber using signal areas of NMR spectrum of PPV: isoprene and OPV: isoprene which are 0.99:99.01 and 2.91: 97.09, respectively. The important effects on the behavior of these materials are their composition, the nature of the dyes, and the loading strain. The PL emission behavior of natural rubber filled with various concentrations of either PPV or OPV between 0% to 4 wt% shows that if the concentration of PL dye is increased, the red shift increases. It is due to the excimer formation. The influences of solid-state tensile deformation on the emission characteristics of natural rubber filled with OPV 3 % and 4 % weight are different from the others, having low concentration of dye. The PL emissions were shifted to shorter wavelength with increasing percentage strain. Their emission changes due to the disruption of the excimers and the emission changes from excimers to isolated excited molecules; therefore a change in color of the emission is possible.

4.2 Introduction

Conjugated polymers attract much interest because they combine the properties of organic macromolecules, such as good mechanical behavior and ease of fabrication, with semiconductor properties that arise from their particular electronic structure. Then conducting organic polymers are a novel class of synthetic metals.

These advanced materials are potentially very interesting for use in photonic and electronic applications (Hiberer *et al.* (1997).

One of the major current research topics is light emission. Many conjugated polymer are highly fluorescent, which makes them suitable for use as laser dyes and active materials in film deformation sensor. Due to the disruption of the excimer of dye molecules, their color emission can be changed. (Crewshaw *et al.*, 2005, and Pucci *et al.*, 2005a).

A number of researches have interested in the photonic and electronic characteristic properties of conjugated polymers. Especially, poly(para-phenylene vinylene) (PPV) and its derivatives (Cirpan *et al.*, 2003).

The purposes of this work are first is to synthesize poly(para-phenylene vinylene) (PPV) and oligo(phenylene vinylene)(OPV). The second is to compare the luminescent properties of PPV grafted on natural rubber as well as OPV grafting on the same host material. The third is to find the optimum amounts of PPV or OPV that is added in the host material to get the good strain sensitive photonic natural rubber from grafting method by using AIBN as the initiator. The final is to study the properties when incorporated photoluminescent additive into natural rubber that may be developed to be special material, which combine photoluminescent with elasticity and other important mechanical properties that are imported by the rubber matrix.

4.3 Experimental

4.3.1 Materials

In this study, natural rubber films used as the matrix for graft copolymerization with PPV and OPV was provided by Rubber Research Institute, 60% DRC. For the synthesis of PPV, the precursor polymer, α , α' xylene chloride (assay \geq 98%), which is commercially available (Aldrich Chemical Co. Ltd.) was used directly. The chemical reagents for OPV preparation OPV were 10-bromo-1-decene (assay \geq 98%), 4-hydroxy-benzyl cyanide (assay \geq 98%), potassium carbonate (assay \geq 99%), dimethylformamide (assay \geq 99.9%), Magnesium sulfate (assay \geq 99.5%), 1,4-dimethoxybenzene (assay \geq 98%), HBr/AcOH 33%,

potassium hydroxide (assay $\geq 85\%$), hexamethylenetetramine (assay $\geq 99\%$), sodium metabisulfide (assay $\geq 97\%$), formaldehyde solution (40 %), 2,5-dimethoxy tetraphthataldehyde (assay $\geq 50\%$ in water), potassium tert-butoxide (assay $\geq 98\%$), 2-(tert-butylamino)ethanol (assay $\geq 99\%$). All of them were purchased from Aldrich Chemical Co, Ltd. In the grafting method, the natural rubber, dyes at various concentrations (0.5, 1, 2, 3, and 4% by weight of natural rubber), and 2,2'-azoisobutyronitrile (AIBN) 0.3% weight of natural rubber were placed under nitrogen gas, stirred and warmed at 70°C for 40 hours. The solution was cast on the glass in air for 40 hours to get copolymer films.

4.3.2 Synthesis of Poly(p-phenylene vinylene) (PPV)

The bis-sulfonium salt 16 g (45.5 mmol) was dissolved in the mixture of 80 ml of water and 45 ml of methanol. The solution was purged with nitrogen for one hour, cooling to 0 °C. 91 ml of nitrogen purged NaOH (45.5 mmol) were added at once with rapid stirring. After stirring for 120 min at 0°C the polymerization was quenched by addition of 0.5 M HCl until pH 6-7 was reached. The neutralized solution was dialyzed against a minimum of 50 l deionized water for 2 days in order to separate the polymer from monomer residues, sodium chloride and oligomeric compounds. The solution from the dialyzed tube was used to prepare free standing films by cast on glass plates in air. Thin films of the precursor polymer were converted to PPV by heating in a vacuum oven at 200°C for 16 hours.

4.3.2 Preparation of PPV Graft on the Natural Rubber by Free Radical Polymerization

The natural rubber, PPV at various concentrations (0.5, 1, 2, 3, and 4% by weight of natural rubber), and AIBN 0.3 wt% of natural rubber were put in a vessel that was placed under nitrogen gas in vessel, stirred and warmed at 70°C for 40 hours. The solution was cast on the glass to get NR-g-PPV film.

4.3.3 Synthesis Oligo(para-phenylene vinylene)

4.3.3.1 Synthesis of (4-Dodecyloxyphenyl) acetonitrile.

A suspension of K_2CO_3 (4.05 g, 29.2 mmol) in dimethylformamide (15 mL) was purged with N_2 for 15 min and heated to 80 °C, and 4-hydroxyphenylacetonitrile (1.47 g, 11.0 mmol) was added. After stirring at 80 °C for 10 min, 10-bromododecene (3.54 g, 14.2 mmol) was slowly added and the suspension was stirred at 70 °C under N_2 for another 4 h. After this time a pale yellow precipitate had formed. The reaction was terminated by pouring the suspension into ice-water (150 mL) and $CHCl_3$ (50 mL) was added to dissolve the precipitate. The organic layer was separated off and the aqueous phase was extracted with $CHCl_3$ (3 x 50 mL). The combined organic layers were washed with H_2O and saturated aqueous NaCl, respectively. The organic phase was dried with $MgSO_4$ and filtered, and the solvent was evaporated in vacuum to yield a pale yellow powder (3.30 g). Recrystallization from EtOH (50 mL) afforded (4-dodecyloxyphenyl) acetonitrile in the form of white crystals.

4.3.3.2 Synthesis of 1,4-Bis(Bromomethyl)-2,5-dimethoxybenzene

To stirred solution of 150 g (1.1 mol) of 1,4-dimethoxybenzene in 750 ml of glacial acetic acid, 65 g (2.2 mol) of paraformaldehyde and 425 ml of HBr/AcOH (33%) were added slowly. The reaction mixture was heated for 1 hour at 50°C and hydrolysed in 3000 ml of water after cooling to room temperature. The residue was filtered off and suspended in 750 ml of $CHCl_3$. This suspension was refluxed for 10 min and filtered off again after cooling to room temperature. The residue was finally dried at 0.1 torr with KOH.

4.3.3.3 Synthesis of 1,4-Dimethoxy-2,5-dicarbaldehyde

To a stirred solution of 87 g (0.6 mol) of hexamethylenetetramine in 2000 ml of toluene, 100 g (0.3 mol) of 1,4-Bis(Bromomethyl)-2,5-dimethoxybenzene was added and refluxed for 4 hours. After cooling to room temperature the yellowish salt was filtered off and dissolved in 1000 ml of $CHCl_3$. The residue was filtered off and again at 0.1 Torr. This salt was dissolved in 3000 ml of water. After the addition of 180 ml of formaldehyde solution (37-39%), the reaction mixture was refluxed for 3 hours. After cooling to room temperature, the crude compound was filtered off and purified by conversion to the

bisulfite adduct. The crude product was suspended in 2000 ml of water. $\text{Na}_2\text{S}_2\text{O}_5$ (250 g, 1.3 mol) was added to the stirred suspension. The reaction mixture was refluxed for 30 min and filtered off to separate by-products. To the stirred solution of the bisulfite adduct, 600 ml (7.4 mol) of conc. HCl was added dropwise. The yellow dialdehyde precipitated and was separated by filtration. Compound was dissolved in 1000 ml of water, filtered off again, and dried at 0.1 torr with P_2O_5 .

4.3.3.4 Synthesis of 1,4-Bis (R-cyano-4-dodecyloxystyryl)-2,5-dimethoxybenzene

2,5-Dimethoxyterephthaldehyde (146 mg, 0.75 mmol) and (4-dodecyloxyphenyl) acetonitrile (500 mg, 1.66 mmol) were dissolved at 70 °C in a mixture of t-BuOH (11 mL) and THF (5 mL). t-BuOK (0.11 mL of a 1 M solution in THF, 0.11 mmol) and n-Bu₄NOH (1 mL of a 1 M solution in MeOH, 1 mmol) were added quickly and an orange precipitate started to form immediately. The mixture was stirred for 15 min at 70 °C, cooled to RT, and poured into acidified methanol (50 mL containing 1 drop of concentrated acetic acid). The resulting precipitate was filtered off, excessively washed with MeOH, and dried in vacuo at 50 °C to yield in the form of orange crystals which is called OPV.

4.3.4 Preparation of OPV Graft on the Natural Rubber by Free Radical Polymerization

The natural rubber, OPV at various concentrations (0.5, 1, 2, 3, and 4% by weight of natural rubber), and AIBN 0.3 wt% of natural rubber were placed under nitrogen gas, stirred and warmed at 70°C for 40 hours. The solution was cast on the glass in air for 40 hours to get NR-g-OPV film (Moroni *et al.*, 1996).

The copolymer moulded by Wabash V50H 50 ton compression molding machine in a press at 50°C for 10 min. The thickness of the moulded films was about 2 mm.

The PPV powder, OPV powder, and copolymer films were analyzed by Perkin-Elmer Pyris Diamond TG/DTA under N₂ flow of 200 ml/min. The samples were weighted at 5-12 mg and put them in the platinum pan. The heating process was conducted from 30-700°C at a rate of 10°C/min. The stability and decomposition temperatures of the samples were determined. The crystallization and melting behaviors of the PPV powder, OPV powder, and copolymer films were measured by

Perkin-Elmer DSC 7 analyzer. Samples were weighted at 5-10 mg and put in aluminium pan. During the crystallization experiment, the specimens were first melted 250°C, and then cooled to room temperature at constant rate of 10°C/min. The specimens were subsequently heated at 10°C/min for the corresponding melting behaviors investigations. The FT-IR spectra of PPV powder, OPV powder, and the grafted copolymer films were collected by using Nicolet Nexus 670 FT-IR spectrometer over a wavenumber range of 4,000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1} to find functional groups and to prove that the dyes were grafted on natural rubber.

Copolymer films were subjected to observe their morphology. The samples were broken by immersing samples in liquid nitrogen. The broken surface of each sample were adhered on the brass stubs by using adhesive tape. All samples were coated with gold were observed by JEOL JSM-5200 scanning electron microscope (SEM) with magnification of 1500/20 kV.

The average molecular weights of the copolymers were determined by using GPC operated at 30-40°C with Styragel column (Walters) in THF solvent. The copolymers solution was prepared by dissolving 10 mg of the copolymer into 5 ml of THF. Inject sample solution of 20 μl was passed through the column using UV detector. The mobile phase is THF flow at 0.6 ml/min. The chromatogram shows that the samples were eluted at time about 17-19 min. The calibration curve prepared from standard narrow molecular weight distribution polystyrene is shown in Appendix A. The copolymer films had to have the same thickness (2 mm) by using Wabash V50H 50 ton compression molding machine to study the photoluminescence property. Influence of either PPV or OPV to fluorescent properties is studied by varying concentrations of dyes by using Fluorescence spectrometer Perkin Elmer LS65 precisely in range 200-900 nm, and scan speed 200 (nm/min). The fix excitation wavelength of each sample was determined by using the pre scan mode. The emission spectra of copolymers were collected under excitation wavelength with excitation and emission slits set to 15 nm. The experiments of PPV-g-NR and OPV-g-NR films were conducted at room temperature using free standing films and the measurements were taken from the front of films by using the excitation wavelengths are 480 and 580 nm for PPV-g-NR and OPV-g-NR, respectively. Moreover, the

influence of stress or strain to photoluminescent properties of samples is studied by varying stress or strain that put on the samples. The draw ratio, defined as the ratio between final and the initial length of the samples, was determined by measuring of ink-marker onto the films before stretching. Vary strain from 50% to 200 %. The initial gauge length was 2 cm. The films were draw from 2 cm to 3, 4, 5, 6 cm with same speed by hand.

4.4 Results and Discussion

4.4.1 Characterization of Poly(para-phenylene vinylene) (PPV)

For the synthesis of PPV, the precursor polymer, α, α' xylene chloride, which is commercially available (Aldrich Chemical Co.) was used directly. The polymerization reactions of the sulfonium salt were carried out under basic conditions and in methanol medium with nitrogen purge at the lowest temperature, 0°C , in order to minimize the subsequent elimination reaction on the polymer.

The initial reaction is a photon abstracting by the base on the benzylic position of the monomer to form the sulfur yield as shown in Figure 4.1.

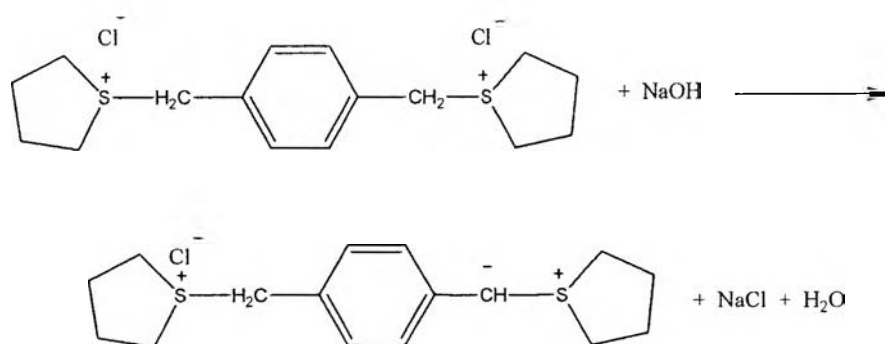


Figure 4.1 Formation reactions.

The yield most likely undergoes a 1,6 elimination reaction to form the p-xylene sulfonium chloride which is the true monomer of the polymerization reaction as shown in Figure 4.2.

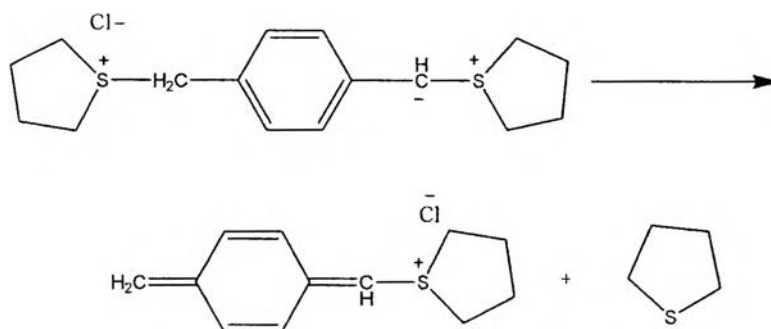


Figure 4.2 1,6-Elimination reaction.

The polymerization was carried out by the addition reaction in Figure 4.3. The polymerization reactions were terminated by the addition of aqueous solution of HCl until pH = 7 was reached and the resulting aqueous solution of the precursor polymers.

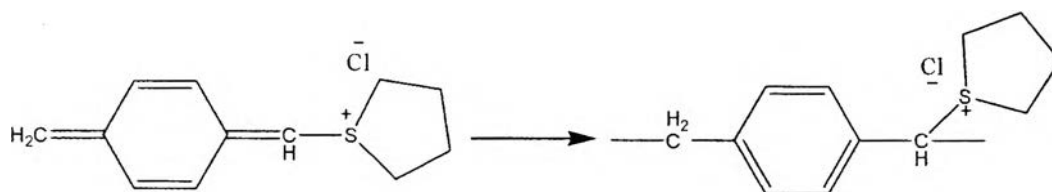


Figure 4.3 Addition reaction.

The obtained polymer was dialyzed for periods of 2-4 days to eliminate both the sodium salt present and the lower molecular weight of by product and unreacted monomers.

After that, conversion of PPV was done by heating to 200°C for 16 hours in the vacuum oven to remove all of the water, organic sulfides and HCl. The resultant homogeneously, dense samples were brownish yellow in color, see Figure 4.4 and 4.5.

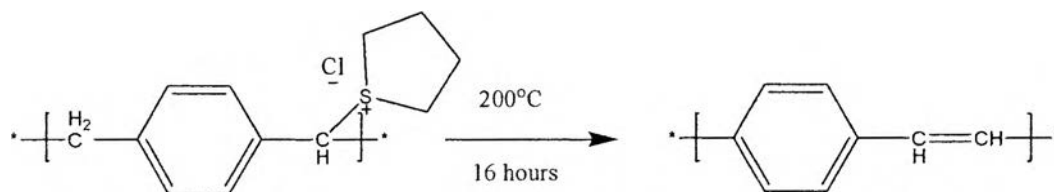


Figure 4.4 Thermal elimination of PPV.

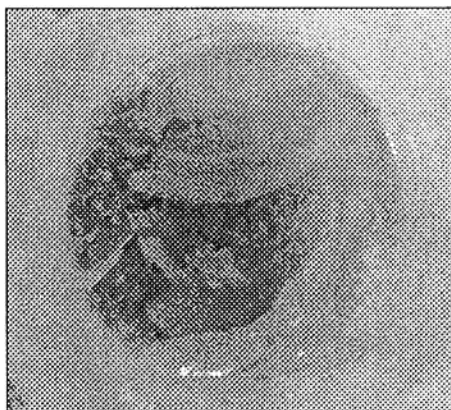


Figure 4.5 The appearance of PPV.

Although the color change is first indication that PPV may be formed, we have to see the FTIR peaks to confirm to PPV formation after the heating (Figure 4.6).

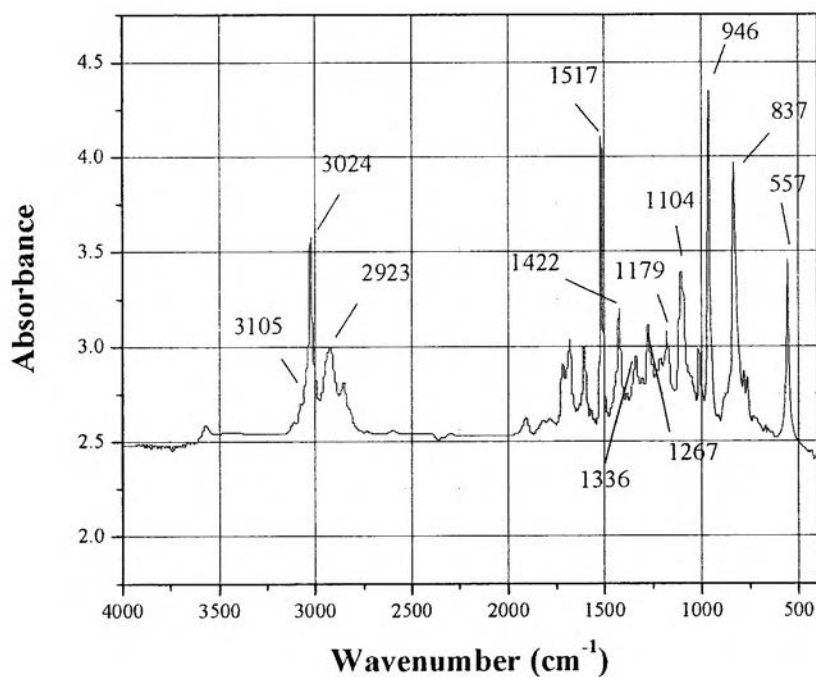


Figure 4.6 FT-IR spectra of PPV.

From Figure 4.6, FTIR spectrum of PPV shows characteristic trans-vinylene C-H out of plane bending peak at 964 cm⁻¹. The p-phenylene C-H in plane

bending shows at about 1270 cm^{-1} . Another is located at 1350 cm^{-1} and corresponds to the C-C phenyl ring stretch seen Table 4.1 (Gmeiner *et al.*, 1993).

Table 4.1 FT-IR absorption band assignment of poly(p-phenylene vinylene)

Frequencies (cm^{-1})	Assignments
3105	Aromatic C-H stretching
3024	Trans-vinylene C-H stretching
2923	C-H stretching from remnant saturated aliphatic groups
1605	C-C ring stretching
1517	
1422	
1336	
1267	C-H in plane bending
1179	
1104	
964	Trans-vinylene C-H out of plane bending
837	Phenylene ring C-H out of plane bending
557	Phenylene out of plane bending

There are three transitions for the precursor of PPV at 151°C , 327°C and 536°C (Figure 4.7). The first one is due to the removal of the solvent from the polymer. The second transition, at 327°C , is related to the elimination reaction, yielding diethyl sulfide and HCl which converts the PPV precursor to PPV. The third transition is attributed to the degradation reaction of the PPV. Figure 4.8 shows the TGA of the PPV exhibits two transitions at 333°C and 526°C . The first transition, at 333°C , is related to the thermal elimination of ethyl sulfide and the second thermal transition, seen at 526°C , is the result of the degradation reaction of PPV (Cirpan *et al.*, 2003).

The TGA results show that when polymers were subjected to stationary heat treatment under vacuum at 200°C for 16 h, they were almost

completely converted to PPV. The endothermic transitions which were responsible for the elimination reaction disappeared after the heat treatment.

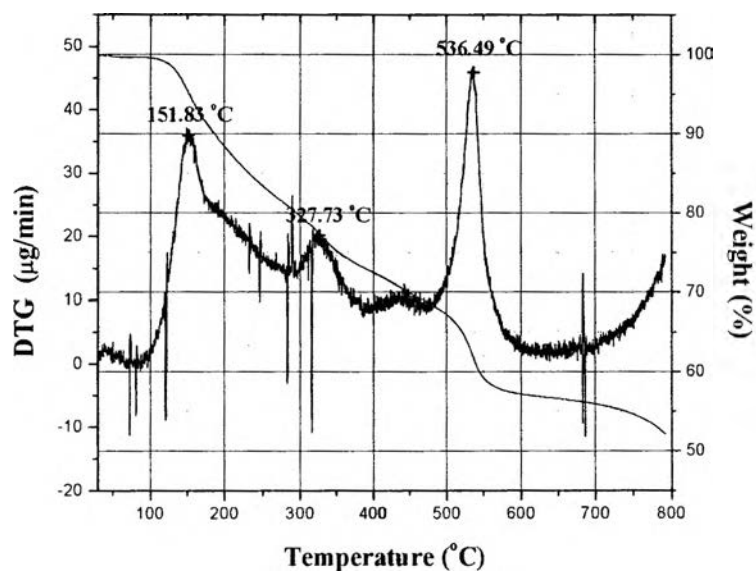


Figure 4.7 Thermal gravimetric analysis curve of the precursor.

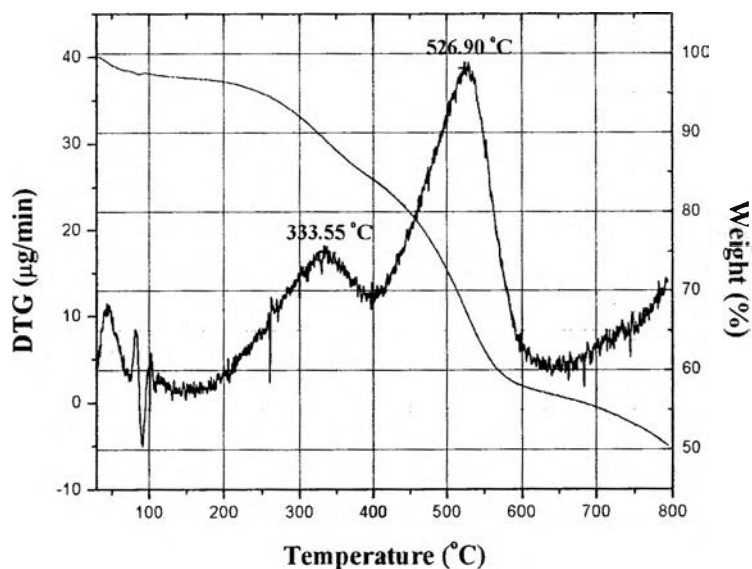


Figure 4.8 Thermal gravimetric analysis curve of PPV.

When the Precursor was heated from 30-250°C under nitrogen gas in the scan rate 10°C/min, it showed endothermic broad peak in the DSC result (Figure 4.9). It is due to the removal of the diethyl sulfide and HCl which converts the PPV

precursor to PPV. Then the DSC result of PPV (Figure 4.10) shows the linear line without the endothermic broad curve. Even though, the specimens were first melted 250°C, and then cooled to room temperature at constant rate of 10°C/min. The specimens were subsequently heated at 10°C/min for the corresponding melting behavior investigations.

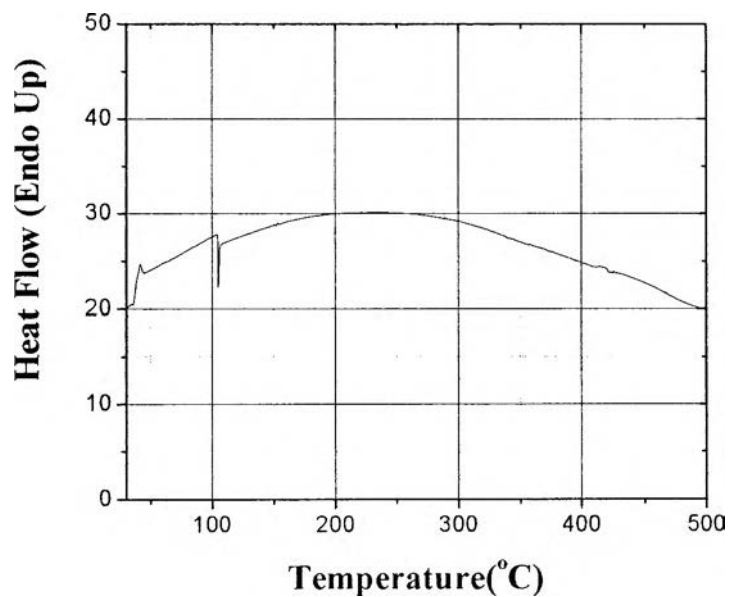


Figure 4.9 DSC thermogram of the precursor polymer. The thermogram was obtained from the scan rate was 10°C/min.

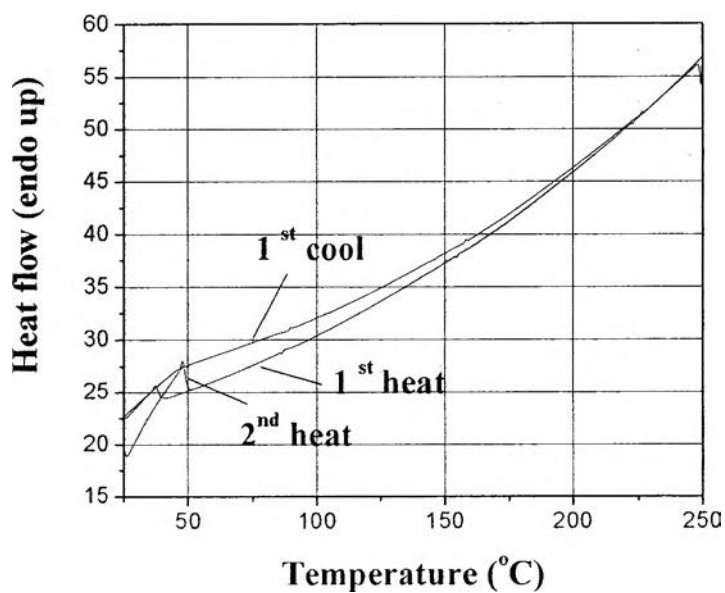


Figure 4.10 DSC thermogram of the PPV. The thermogram was obtained from the scan rate was 10°C/min.

The PPV precursor cast onto the glass substrate for preparing the free stranding film, and then heat treated at 200°C. The PPV film is obtained by peeling off the substrate, and then is milled into small pieces of sample of several ten microns. From Figure 4.11, the average particle size of milled PPV powder is about 6 μm .

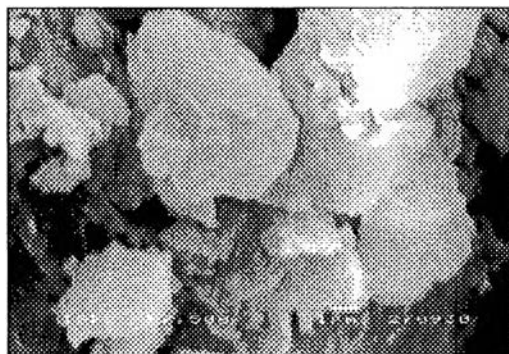


Figure 4.11 SEM micrograph of PPV.

Photoluminescence emission characteristics of the PPV are shown in Figure 4.12. The excitation and emission spectra show that PPV solution absorbs light at 373 nm. It is the fixed wavelength used in emission mode to find the emission wavelength of PPV solution. PPV solution emits in blue light region at 433.5 nm.

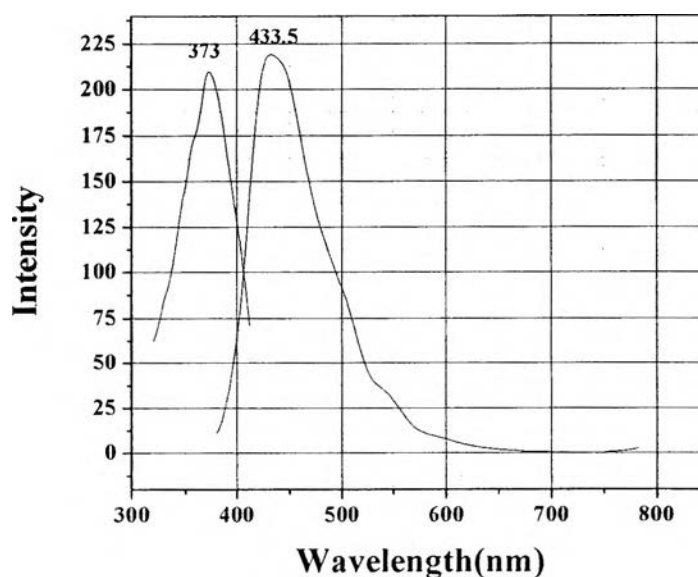


Figure 4.12 PL spectra of PPV solution in toluene, $\lambda_{\text{ex}} = 373 \text{ nm}$.

4.4.2 Characterization of Oligo(para-phenylene vinylene)

The cyano-OPV employed in this study can be synthesized by 3 steps. Firstly, the allyl bromide was added to a suspension of cyanide phenol derivative and K_2CO_3 in acetone at room temperature (Figure 4.13). The reaction mixture was stirred at $70^\circ C$ for 4 hours, and the precipitate was filtered off and the filtrate was evaporated to dryness in vacuum (Sckizaki *et al.*, 2003).

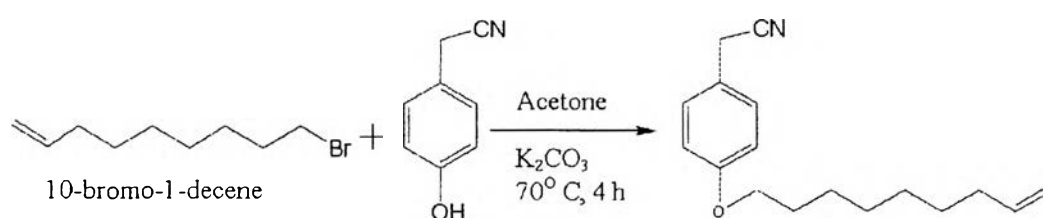


Figure 4.13 Formation reaction of (10-dodecyloxyphenyl) acetonitrile.

The 1,4-dimethoxybenzene was bisbromomethylated in glacial acetic acid solution with paraformaldehyde and hydrogen bromide to obtain a desired compound. By this method (Figure 4.14) where chloromethylation leads to the formation of carcinogenic byproduct could be avoided. The terephthalaldehyde could be obtained.

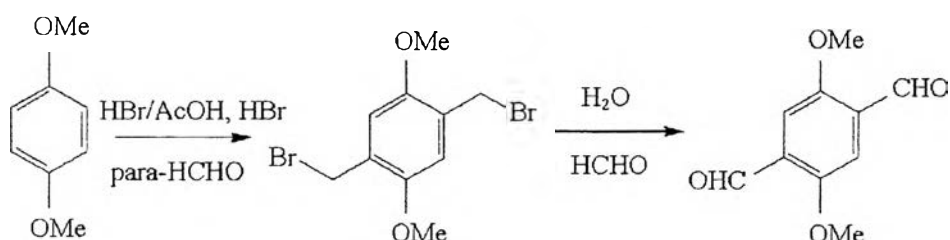


Figure 4.14 Formation reaction of terephthalaldehyde.

The final step, 2,5-dimethoxy terephthalaldehyde and (10-dodecyloxyphenyl) acetonitrile were dissolved at $70^\circ C$ in a mixture of *t*-BuOH and THF. t -BuOK and n -Bu₄NOH were added quickly and an orange precipitate started to form immediately. t -BuOK and n -Bu₄NOH are bases. When t -BuOK is added a

proton will be removed and this why it changes color. When $n\text{-Bu}_4\text{NOH}$ is added the proton has already been removed so it will not change color. The mixture was poured into acidified methanol to neutralization. The resulting precipitate was dried at 50°C to yield the cyano-OPV dyes seen in Figure 4.15 (Crenshaw *et al.*, 2003, and Lowe *et al.*, 2002).

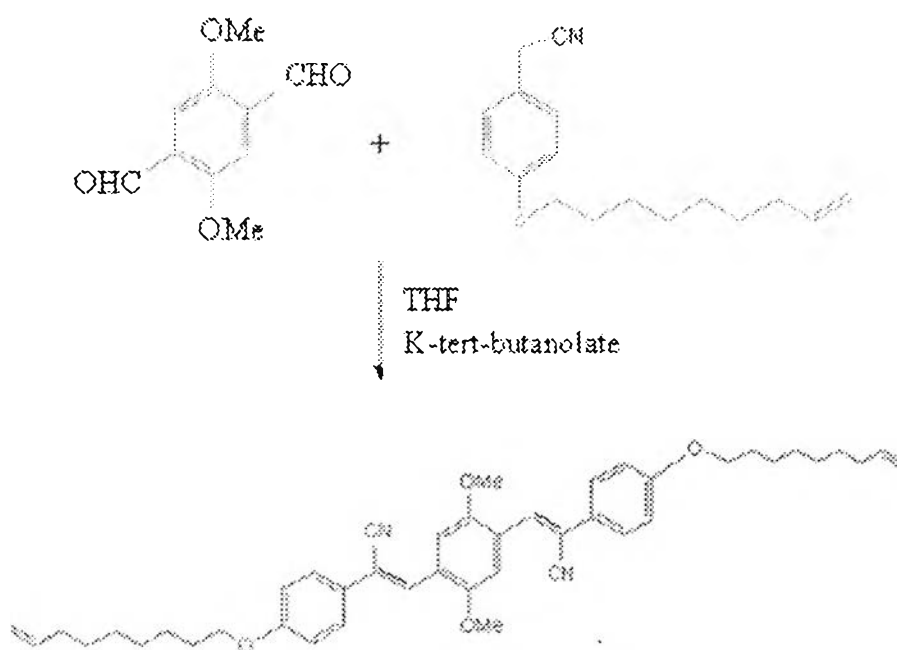


Figure 4.15 The reaction formation of cyano-OPV.

The identity of the synthesized compounds was verified by using FT-IR spectrophotometer and NMR spectrometer. Figure 4.16 and Table 4.2 show the FT-IR spectrum of oligo(para-phenylene vinylene) on KBr pellet. The trans-vinyl C-H stretching exhibits a peak at 3024 cm^{-1} . C=C or aromatic rings is a weak absorption near 1680 cm^{-1} . Medium to strong absorptions in the region $1650\text{-}1450\text{ cm}^{-1}$ often imply an aromatic ring (The C-C ring stretching shows peaks at 1677 , 1495 , 1405 cm^{-1}). Nitrite ($\text{C}\equiv\text{N}$) shows a weak absorption near 2250 cm^{-1} . The C-O absorption shows near 1125 cm^{-1} (Kawanara *et al.*, 2003).

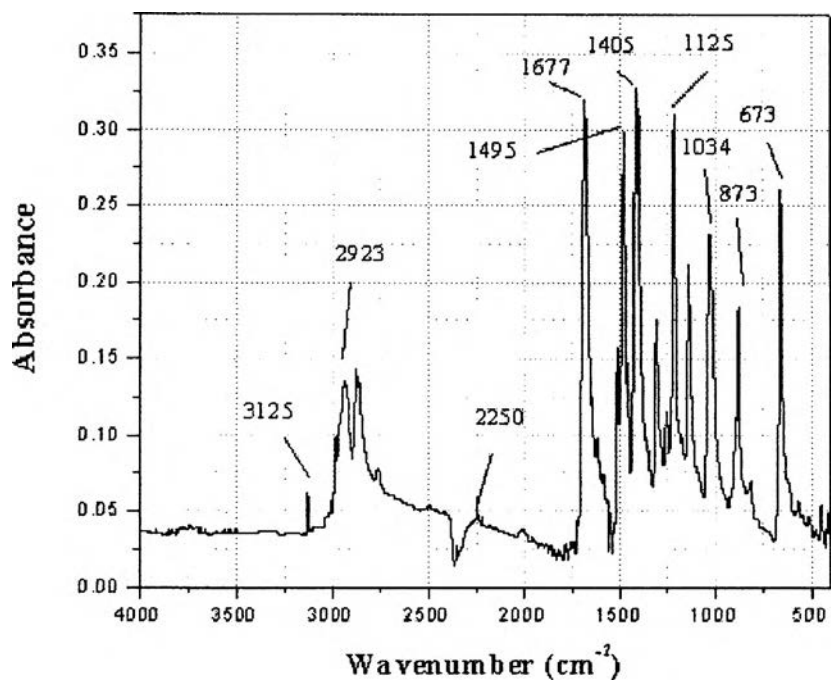


Figure 4.16 FT-IR spectrum of oligo(para-phenylene vinylene).

Table 4.2 FT-IR absorption band assignment of oligo(para-phenylene vinylene)

Frequencies (cm ⁻¹)	Assignments
3125	Aromatic C-H stretching
2923	C-H stretching from remnant saturated aliphatic groups
2250	Nitriles C≡N
1677	C-C ring stretching
1495	
1405	
1125	C-O
1034	Trans-vinylene C-H out of plane bending
873	Phenylene ring C-H out of plane bending
673	Phenylene out of plane bending

The ^1H NMR from Appendix B can be used to prove the structure of synthesized OPV. The signals show at 7.42 (ArH+CH=CCN), 7.2 (ArH), 6.9 (ArH), 3.95 (O-CH₃), 3.87 (O-CH₂), 1.7 (CH), and 1.57-1.33 ppm (=CH₂). When compared with 1,4-Bis(α -cyano-4-methoxy styryl)-2,5-dimethoxybenzene (Lowe *et al.*, 2002), the difference is 1.57-1.33 corresponding to =CH₂, which came from 10-decene.

The thermal properties of OPV were studied using the differentially scanning calorimeter (DSC) at heating rate 10°C/min see in Figure 4.17. Upon heating, a glass transition of OPV did not show. The melting transition temperature at the maximum heat flow was determined to be about 198.5°C. The melting point of OPV is lower than 1,4-Bis(α -cyano-4-methoxy styryl)-2,5-dimethoxybenzene (Lowe *et al.*, 2002) that came from the aliphatic chain made the efficiency of packing were lower.

Thermal gravitation analysis reveals that OPV is thermally degraded with 3 steps at about 135, 266, and 434°C as shown in Figure 4.18. The first one may be due to the solvent removal, the second transition is to get rid of aliphatic chain, and the last transition reveals the degradation of OPV.

The onset degradation temperature of natural rubber is 350°C. Therefore natural rubber was chosen as a polymer to graft by PPV and OPV for many reasons. First, natural rubber can be dissolved in common solvents such as chloroform, toluene, and water. For PPV and OPV, toluene solvent was chosen to be solvent because PPV, OPV and natural rubber are soluble in toluene which facilitates grafting. Second PPV and OPV can withstand temperature up to 70°C, which is required because of the grafting process (Camillo *et al.*, 2005).

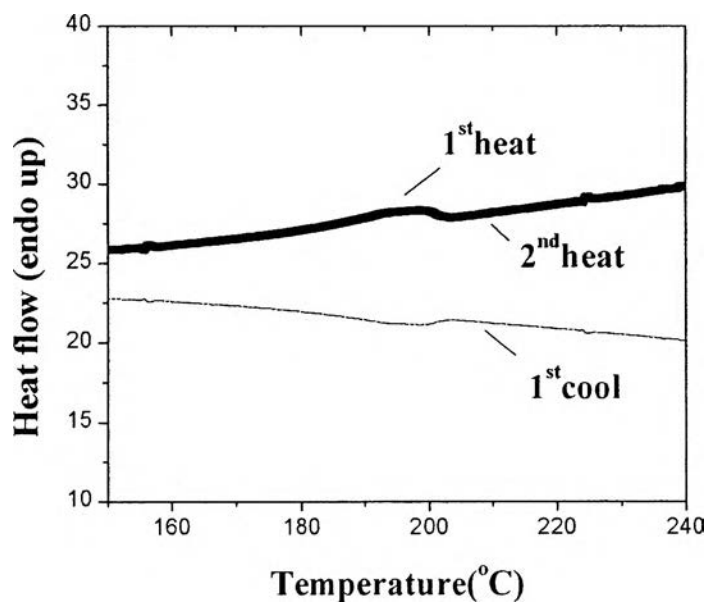


Figure 4.17 DSC thermogram of the OPV obtained from the scan rate $10^{\circ}\text{C}/\text{min}$ under nitrogen gas atmosphere.

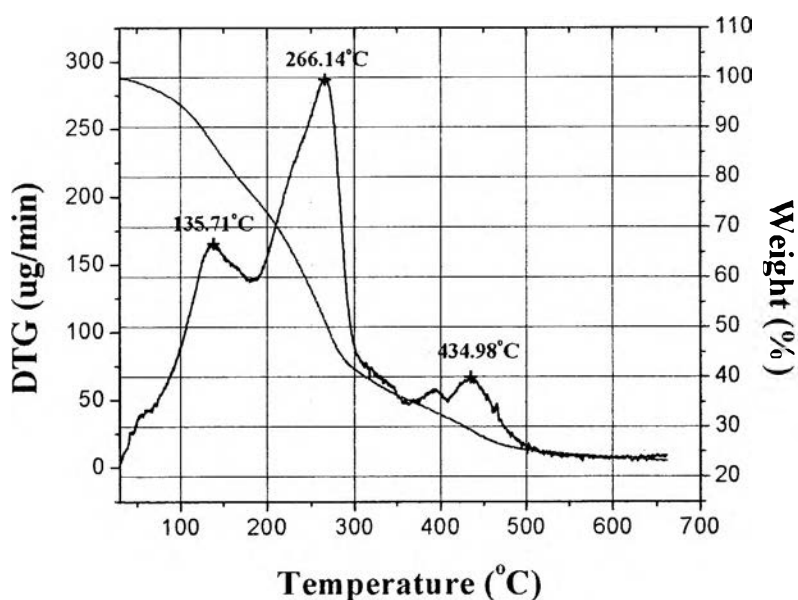


Figure 4.18 Thermal gravimetric analysis curve of OPV under nitrogen gas atmosphere.

The SEM photograph of synthesized OPV is shown in Figure 4.19. It shows that the original particles of OPV are irregular shaped. The given color of OPV is green-yellow.

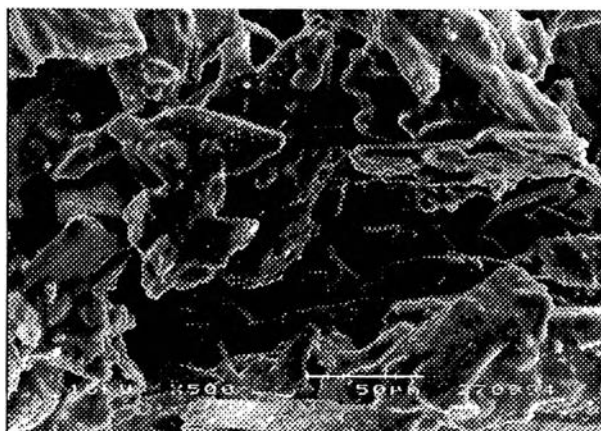


Figure 4.19 SEM micrograph of the surface of OPV.

The optical properties of this dye were studied in detail by steady-state PL spectroscopy. The results of Lowe *et al.* (2003) showed the maximum absorption peak of 1,4-bis(α -cyano-4-methoxystyryl)-2,5-dimethoxybenzene at 436 nm. As expected, the substitution of a *n*-alkene chain to the benzene ring caused small red shift, which features a maximum at 450 nm, see Figure 4.20.

The PL spectrum of OPV shows the absorption band at 447 nm and the emission appears in the green region with the highest intensity at 501 nm (by using the excitation wavelength at 450 nm). The emission is slightly blue-shifted when compared to 1,4-Bis(α -cyano-4-methoxy styryl)-2,5-dimethoxybenzene which shows maximum at 506 and 538 nm (by using the excitation wavelength at 450 nm).

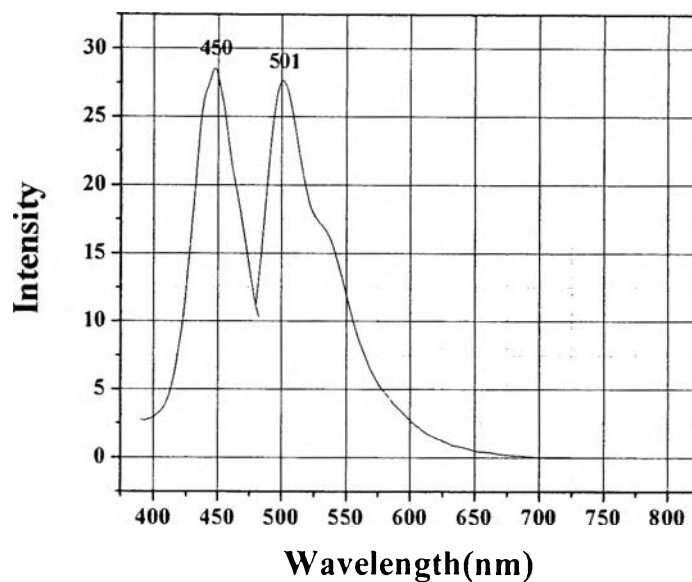


Figure 4.20 PL excitation and emission spectra of OPV solution in toluene, λ_{ex} = 450 nm.

4.4.3 Characterization of PPV Grafted on Natural Rubber by using PPV

The copolymer of PPV grafted natural rubber (see Table 4.3) was characterized by both FT-IR and NMR.

Table 4.3 Amounts of components used in copolymer preparation

Sample PPV content (g)	Toluene (ml)	NR latex (g)	AIBN (g)	Drying temperature (°C)
0.05	500	10	0.3	50
0.1	500	10	0.3	50
0.2	500	10	0.3	50
0.3	500	10	0.3	50
0.4	500	10	0.3	50

The FT-IR was used to study the functional group in the grafted natural rubber. The NMR was used to determine the mole ratio of dye and isoprene in grafted natural rubber. The IR spectra of natural rubber (Appendix C), natural rubber grafted PPV (Figure 4.21) at various PPV concentrations, and PPV, focused on the range of wavenumber 400-4000 cm^{-1} . The absorbed bands of PPV grafted natural rubber show clearly absorbed band of the principal peaks corresponding to isoprene functional groups of natural rubber are 3033, 2961, 2927, and 2855 cm^{-1} (=C-H stretching, C-H stretching of CH_3 , C-H stretching of CH_2 , and CH_3 , respectively) but not seen easily the absorption band of PPV (trans-vinylene C-H out of plane bending peak at 964 cm^{-1} . The p-phenylene C-H in plane bending shows at about 1270 cm^{-1} . The other one is located at 1350 cm^{-1} and corresponds to the C-C phenyl ring stretch). From this reason, we have to use NMR to clarify the present of PPV grafted on natural rubber.

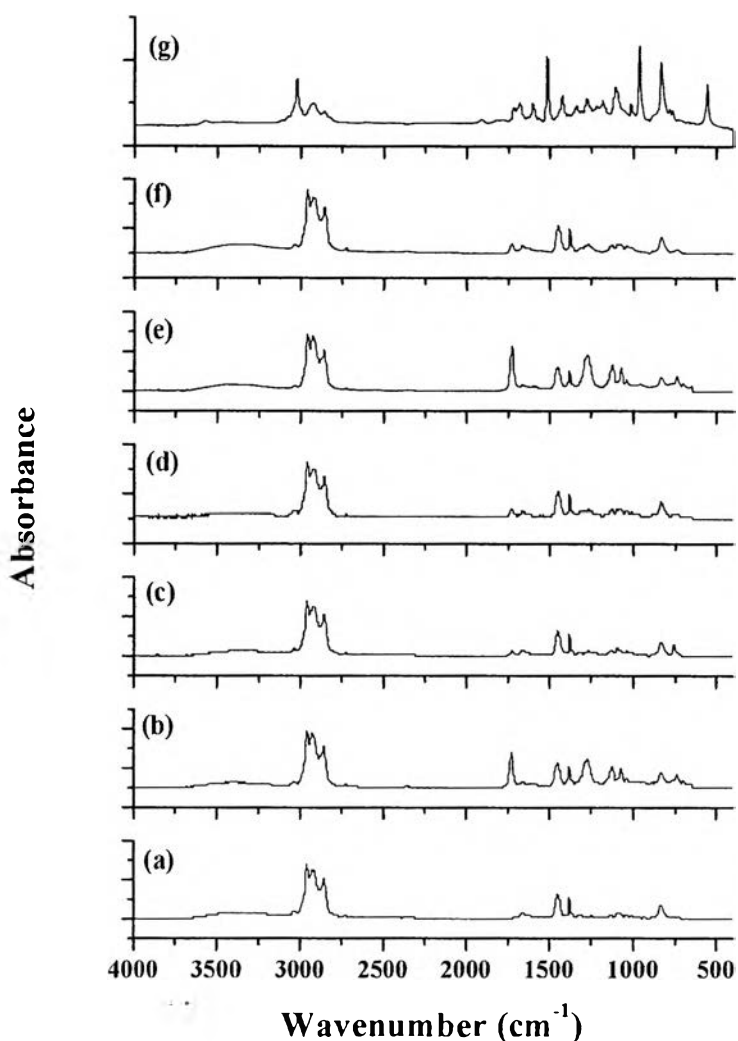


Figure 4.21 FTIR spectra of (a) NR, NR-g-PPV (b) 0.5 wt%, (c) 1 wt%, (d) 2 wt%, (e) 3 wt%, (f) 4 wt%, and (g) PPV.

The copolymer composition of natural rubber and PPV was determined by ^1H NMR. The sample was dissolved with CDCl_3 .

From Appendix D, the appearance of natural rubber, the following ^1H NMR (CDCl_3) peaks were assigned at 5.2 ppm for $\text{C}=\text{CH}$ proton of isoprene, 2.10 ppm for $(\text{CH}_2)_2$, and 2.10 ppm for CH_3 (Oliverira *et al.*, 2005). The occurrence of PPV peaks show at 7.2, 1.1, and 0.7 ppm. The PPV peaks indicate that PPV groups have been bound to natural rubber (Table 4.4).

Table 4.4 The ratio of PPV grafted natural rubber calculated from signal areas of NMR spectrum

Sample	Signal area per H		Mole Ratio	
	7.2 ppm	5.2 ppm	PPV	Isoprene
3 wt%PPV	0.01	1	0.99	99.01

* 7.2 ppm is ArH (=1H), 5.2 ppm is C=CH (=1H)

The TGA data show that graft copolymer acts as natural rubber more than PPV (Figure 4.22). In all of case mass loss starts below 100°C which could be attributed to water evaporation. In Figure 4.22 the large amount of mass is loss before 370°C. The onset degradation temperature of graft copolymer is slightly shifted to lower than the natural rubber. It means that thermal stability of the graft copolymer not greatly changed by the small amount of PPV.

Moreover, the DTG spectra in Figure 4.23 show that the copolymers exhibit slight shift of the highest decomposition temperatures up to about 4°C in comparison to that of with one of natural rubber film.

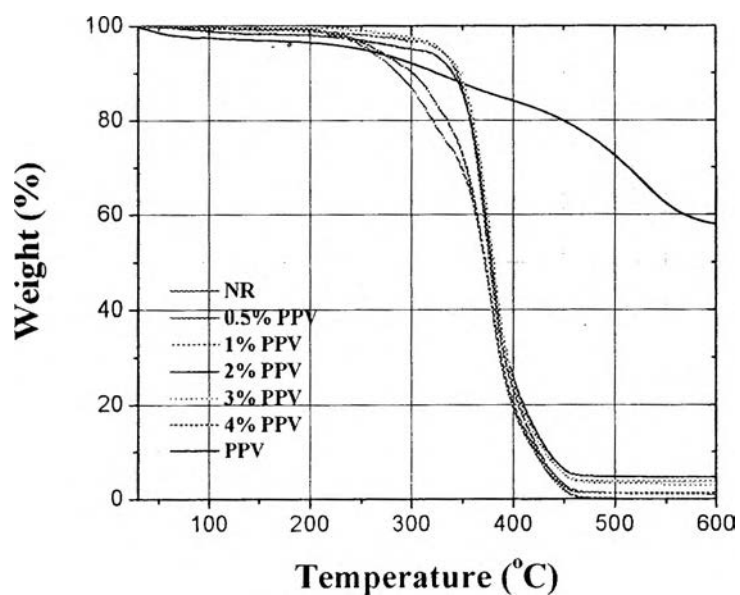


Figure 4.22 %TG spectra of NR, NR-g-PPV 0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, and PPV.

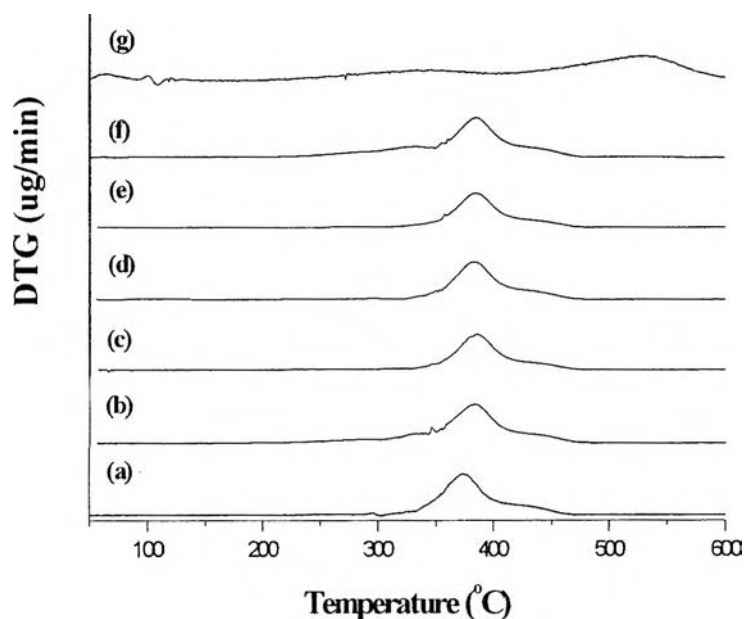


Figure 4.23 DTG spectra of (a) NR, NR-g-PPV (b) 0.5 wt%, (c) 1 wt%, (d) 2 wt%, (e) 3 wt%, (f) 4 wt%, and (g) PPV.

From results of Camilo *et al.* (2005), the glass transition temperature of natural rubber is -67°C while T_g of the copolymer added PPV 3%wt is about -65.9°C (shown in Figure 4.24). This elevation of T_g is attributed to the restriction on chain mobility of the presence in the bulky grafted PPV on the natural rubber molecules.

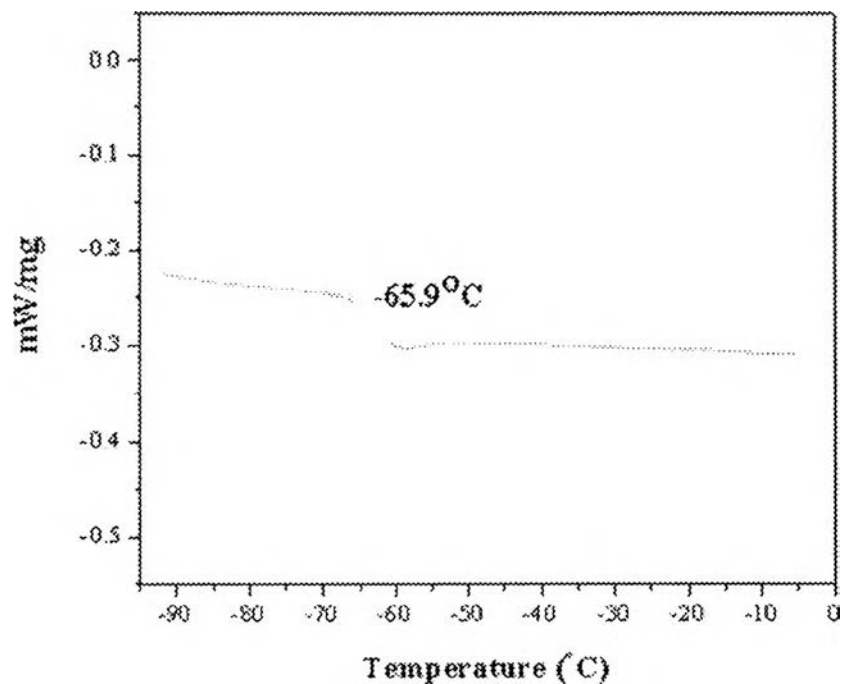


Figure 4.24 The DSC result of natural rubber grafted with PPV 3 wt%.

The excitation spectra in Figure 4.25, the main peaks of all copolymer are centered in the 480 nm region. Therefore, the excited wavelength of natural rubber filled with PPV is 480 nm. In the excitation spectra shown in Figure 4.25, the maximum absorbance of natural rubber at 450 nm, but the copolymers of natural rubber and PPV have the maximum absorbance at 450 and 480 nm. From these results we can know the specific wavelength to excite the copolymers.

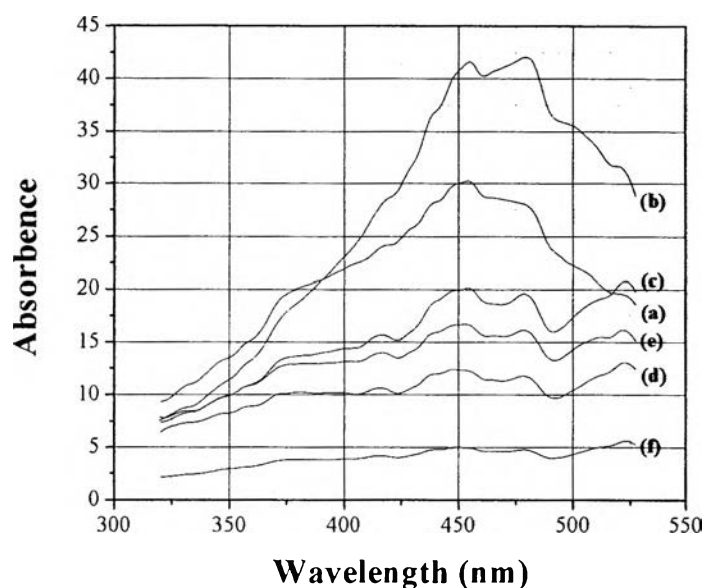


Figure 4.25 Excitation spectra of natural rubber grafted with PPV (a) 0%, (b) 0.5%, (c) 1 %, (d) 2%, (e) 3%, and (f) 4 wt%.

Generally, PPV emits fluorescence in yellow-green range. The yellow attributed at about 550 nm wavelength, while the green at 520 nm (Zeng *et al.*, 2005). With increasing the amount of PPV, obviously red shift and broadening of peak width for peak at 550 nm to be 593 nm, as well as the decreasing of peak intensity can be seen. They show the same results as ones of Crenshaw *et al.*, (2005) and Pucci *et al.*, (2005b). They found that upon increasing the concentration of dye in the blends, the emission spectra displayed a modest bathchromic shift, increasing λ_{\max} . Even though they used different dye types, Pucci *et al.*, (2005a) used bis(benzoxazolyl) stilbene, Crenshaw *et al.*, (2005) used the same route with this study. All of cases showed that the red shifted came from the excimer formation.

At 0.5 wt% of PPV (Figure 4.26), the emission centered at 546 nm that is in the yellow-green region. For the higher percentage of PPV, the second emission peak is occurred at 587 nm (shown red color). The maximum shift occurs at 4 wt% loading to natural rubber. Figure 4.26 suggests that without PPV, NR has no clear photoluminescence while pure PPV emits at 603.5 nm. It is intensity to note that the PPV-g-NR shows photoluminescence (after excited by 450 nm) at the range of 500-650 nm (green to red) dependent on amount of grafted PPV. There is only one PL at 546 nm for 0.5 wt% of PPV grafted NR and then another peak developed at

about 585.5 nm. This peak become red shift with PPV content and closed to PL of pure PPV. Not only has red shift occurred at 585 nm but also at 546 and 520 nm. This suggests that the conjugated length increase with PPV content and more PL like PPV.

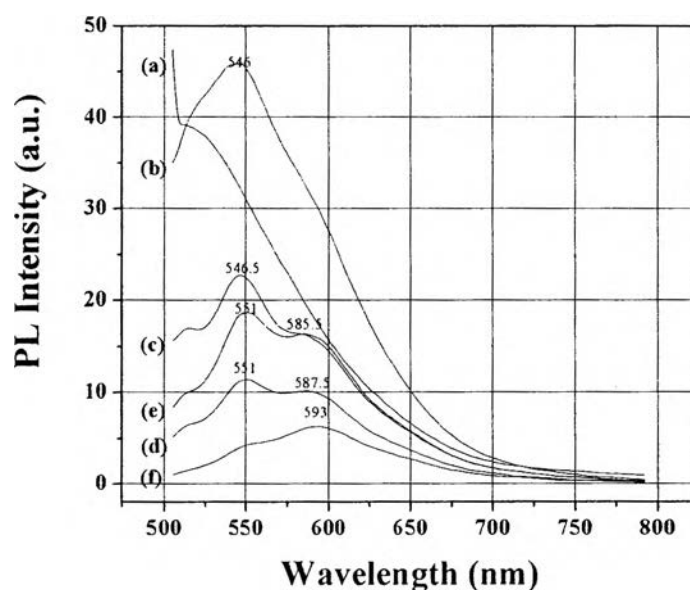


Figure 4.26 Emission spectra of natural rubber grafted with PPV (a) 0%, (b) 0.5%, (c) 1 %, (d) 2%, (e) 3%, and (f) 4 wt%.

From the stress-strain curve, the young modulus of natural rubber that can be calculated by using slope of the linear region was 0.01 ± 0.49 MPa. The films were broken at 447 ± 8 percentage strain. The tensile stress-strain test of our rubber gives different results from others. Camillo *et al.*, 2005 found that the elongation of NR cast films is practically up to 700%. The rupture point for NR is 1.4 ± 0.5 MPa.

In the studying of effect of strain to the fluorescence characteristics, the percentage strains to use in this study in range 0-200 %. They cover the elastic region, and plastic region. Effect of percentage strain on the fluorescence emission of the copolymers was investigated. From Figure 4.27, an increase in percentage strain ranging from 0 % to 200 % results in red-shifts of the emission. The strain induced

red shift amounts to about 549.5 nm at 150 %, and then the blue shift appears at 200 % strain caused by pressure effects on the aggregation of dyes molecules.

There is the influence of solid-state tensile deformation on the emission characteristics of the copolymer films. Figure 4.27 shows a broad emission of 0.5 wt% PPV grafted natural rubber centered at 546 nm before stretching. A small stretching clearly induces two emission spectra at 546 and 590 nm. The latter peak starts like a shoulder and developed to a broad peak with increasing % strain to 200%.

The changing of PL emission with strain can be clearly seen in Figure 4.28 showing the shift of the PL center wavelength vs. percentage strain for natural rubber filled with PPV 0.5 wt%. The red shift increases with the increasing of strain. Until the adequate strain, the separation of excimer molecule is occurred. This suggests that the conjugation length becomes shorter due to too much stress applied to the specimen. Moreover, 200% strain induces crystallization (Lin *et al.*, 2004) forcing the breaking of conjugation length and the plastic flow region allow some relaxation shorten the conjugation length. This suggests that increasing %strain induce similar phenomena, red shift like increasing % PPV (Figure 4.26).

The tenacity results can be found in research of Yang *et al.*, (1999) who used poly(2-methoxy-5-(2-ethylhexoxy)-p-phenylene vinylene. to study the effect of pressure in variety of polymer media. They found that the emission band is shifted to lower energy with increasing pressure, but above 30 kbar there is some bands showing a small blue shift due to the strain induced crystallization (Lin *et al.*, 2004). When the external force is high and film thickness reduces enough, the aggregated dyes are compressed to break apart.

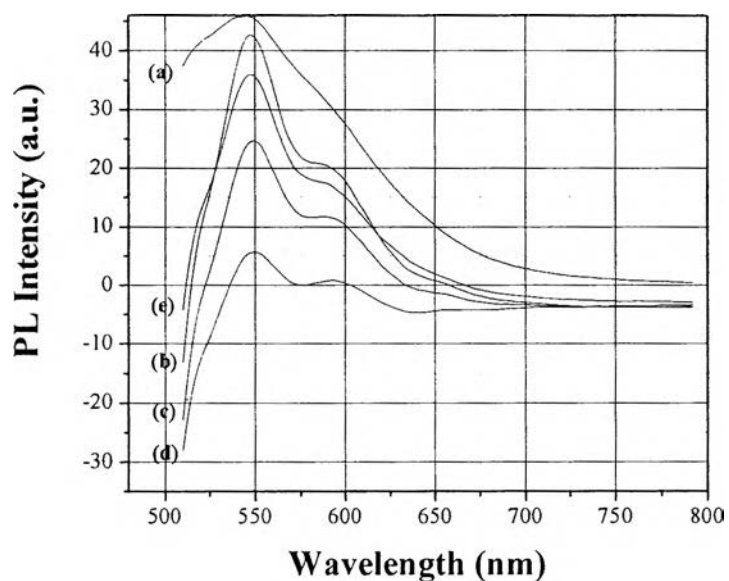


Figure 4.27 Emission spectra of natural rubber grafted with PPV 0.5 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and(e) 200%.

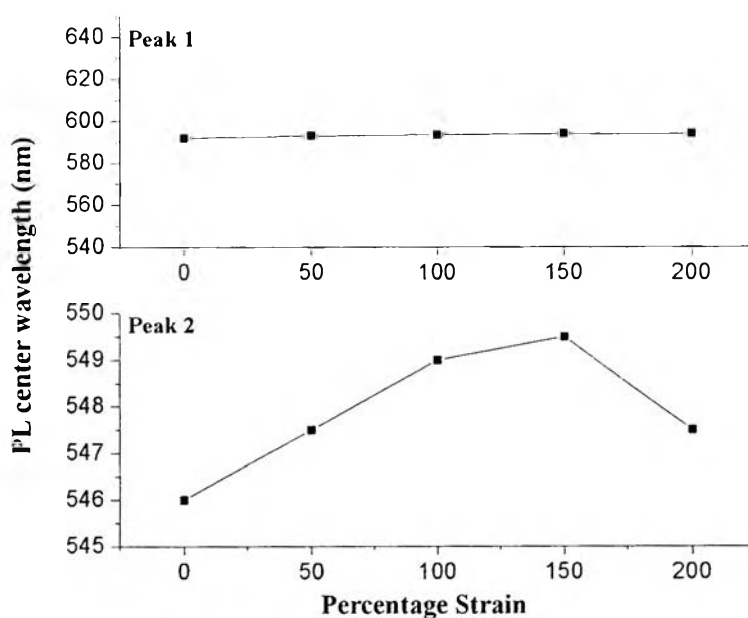


Figure 4.28 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with PPV 0.5 wt%.

Figure 4.29-4.30 show emission spectra of NR-PPV 1 wt% after stretching to 50-200%.

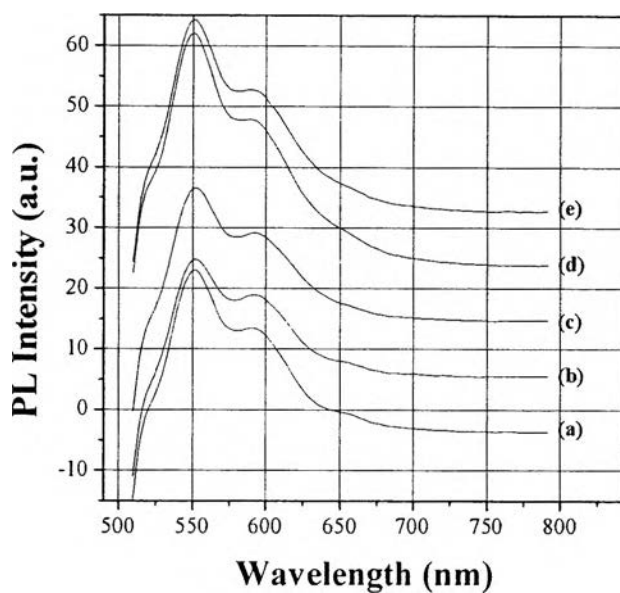


Figure 4.29 Emission spectra of natural rubber grafted with PPV 1 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and(e) 200%.

The bands are, in general, 546.5 and 593 nm and do not largely change in width significantly with percentage strains. There are shifts to lower energy with increasing strain of 50-100%, but above 100 %, there is a small blue shift (Figure 4.30).

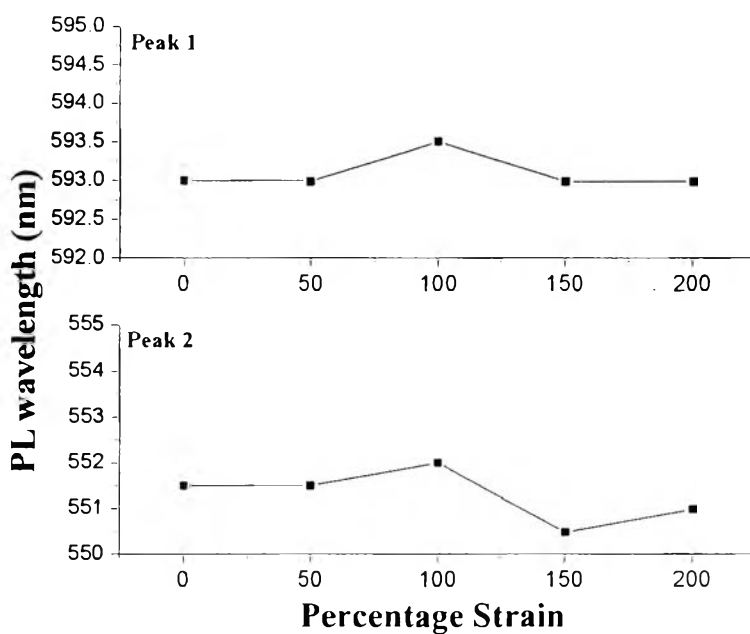


Figure 4.30 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with PPV 1 wt%.

Figures 4.31 and 4.32 demonstrate that solid-state tensile deformation has a pronounced effect on the emission characteristics. When the films are stretched to a draw ratio 100%, the samples display good contrast between stretched and unstretched samples. The blue shifts are increase at draw ratio 100-150%.

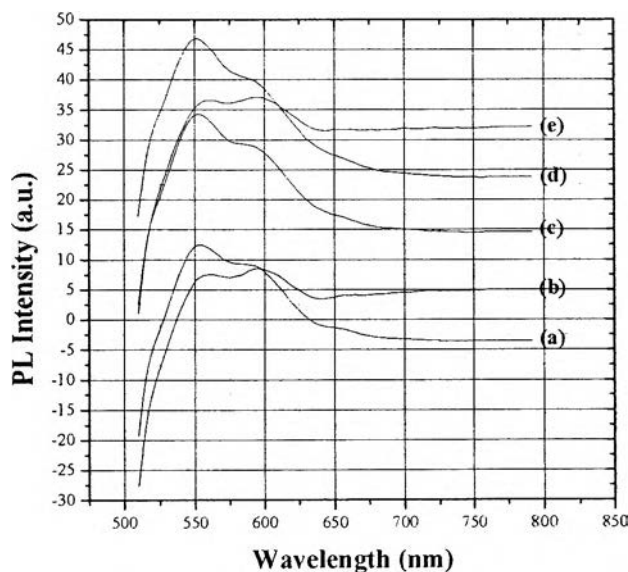


Figure 4.31 Emission spectra of natural rubber grafted with PPV 2 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and(e) 200%.

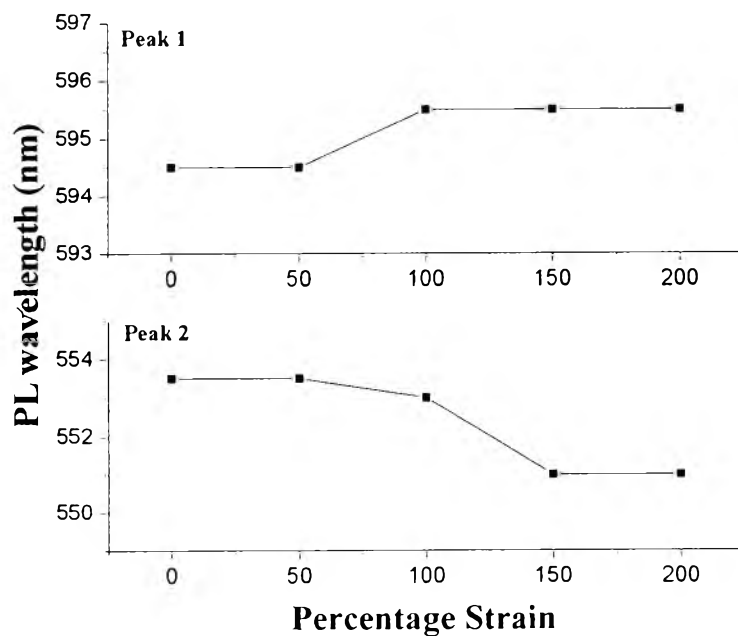


Figure 4.32 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with PPV 2 wt%.

Figure 4.33-4.34 show emission spectra of NR-PPV 3 wt% after stretching to 50-200%. The red shifting of natural rubber grafted with PPV 3% still shows similarly as the above samples. Firstly, they show red shift at small stress, and then show blue shift at draw ratio 50%. But the changing shows in range 2-3 nm which are not easy to see by human eye.

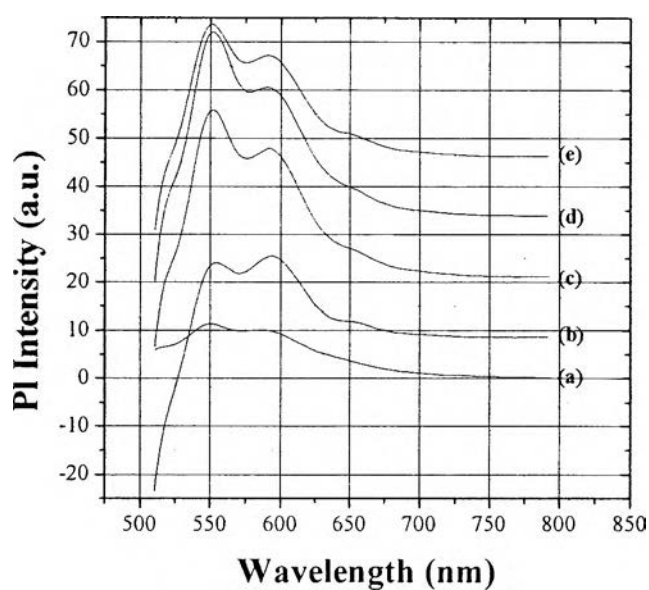


Figure 4.33 Emission spectra of natural rubber grafted with PPV 3 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and (e) 200%.

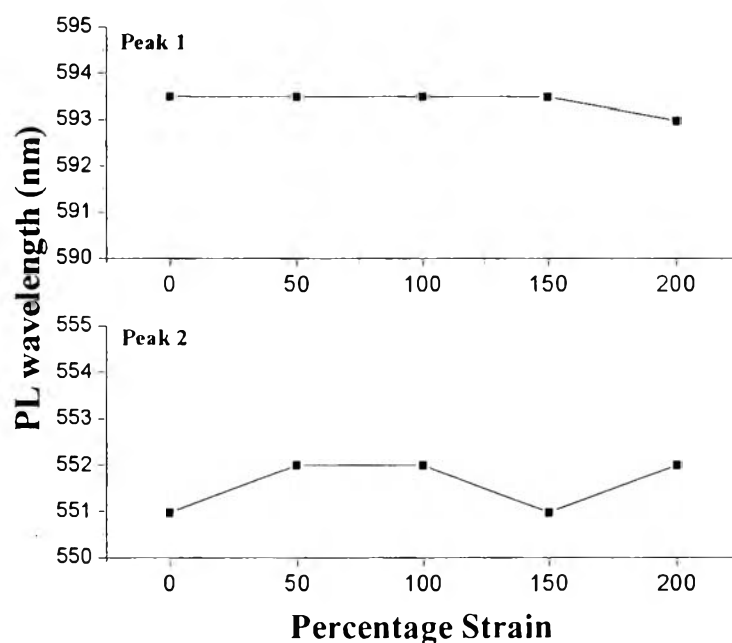


Figure 4.34 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with PPV 3 wt%.

Upon stretching the emission behaviors of natural rubber filled with PPV 4% weight was different from others, see Figure 4.35-4.36. Although they show the red shift at the first time of stressing and the blue shift at draw ratio 100%, but they do not show the red shift again at the higher strain. That means the aggregations of dye molecules are broken, even though the stress leads the chains to a high degree of linearization. This force may break the conjugation length.

Many researches investigated the effect of high-pressure to the luminescence properties of PPV black bone. They found that the applying pressure to the conjugated length may vary. Zeng *et al.* (2005a), and Tikhoplave *et al.* (1999) suggested that favorite form is planar chain for occupying the least volume at high pressure. The effect of pressure is to increase chain planarity by reducing the out-of-plane rotation. In other words, the density in PPV chains increase with pressure.

The PL red shift can be explained by conjugation model. The conjugation model is based on the free electron theory of conjugated molecules introduced by following equation:

$$E_0 = A + B/L$$

Where E_0 is energy band gap, L is conjugation length of a chain, and A , B are constants. It is seen that PL red shift at the high pressure is due to the elongation of the conjugation length. This may be the same reason why red shift occurred when we apply strain to the copolymers.

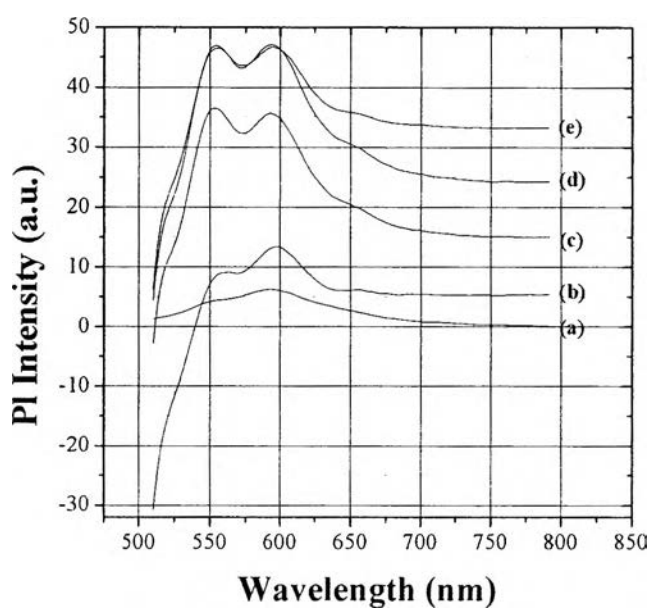


Figure 4.35 Emission spectra of natural rubber grafted with PPV 4 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and(e) 200%.

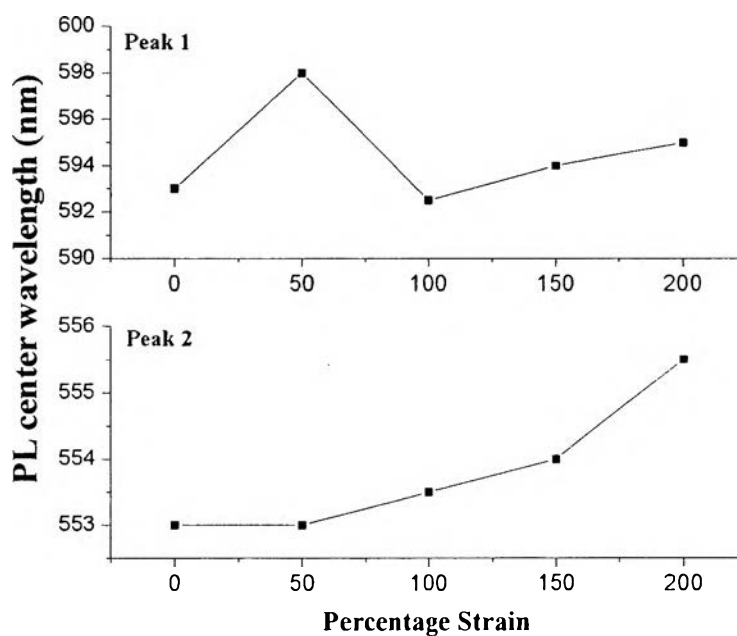


Figure 4.36 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with PPV 4 wt%.

The grafting method that uses the heating and stirring may effect to the molecular weight. The GPC results show chromatogram of copolymers in Figure 4.37. The Figure 4.37 suggests that increasing the PPV to graft on natural rubber leads the higher molecular weight of copolymer. They can be assumed that the grafting is success and heating and stirring does not destroy the polymer chains.

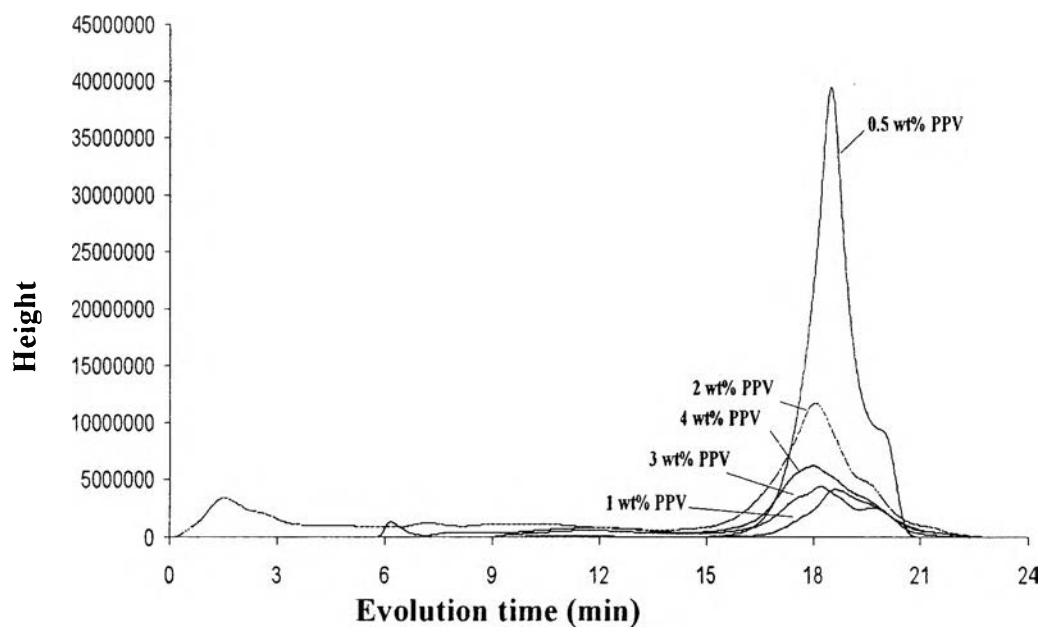


Figure 4.37 The chromatograms of PPV-g-NR copolymer .

4.4.4 Characterization of OPV Grafted on Natural Rubber

The characterizations of OPV grafted on natural rubber with the different amount of OPV (Table 4.5) are the same as the previous copolymer.

Table 4.5 Amounts of components used in copolymer preparation

Sample OPV content (g)	Toluene (ml)	NR latex (g)	AIBN (g)	Drying temperature (°C)
0.05	500	10	0.3	50
0.1	500	10	0.3	50
0.2	500	10	0.3	50
0.3	500	10	0.3	50
0.4	500	10	0.3	50

Figure 4.38, FT-IR spectra recorded on natural rubber and copolymer at various concentration of OPV, which were prepared by using toluene as solvent and deposited on glass substrates. IR spectrum (a) in Figure 4.38 is for absorption of NR showing its characteristic peaks at 1960, 1660, 1450, and 835 cm^{-1} referring to $-\text{CH}$ stretching, $\text{C}=\text{C}$ stretching, CH_2 stretching, $=\text{CH}_2$ stretching, respectively. The spectrum (g) is the IR absorption of pure OPV. Their characteristic peaks are at 3024, 2250, 1677, 1495, and 1125 cm^{-1} referring to the trans-vinyl C-H stretching, $\text{C}\equiv\text{N}$, $\text{C}=\text{C}$ stretching, C-H stretching of aromatic ring, and C-O bending, respectively. The NR-g-OPV copolymers at various content of OPV show spectra like that of NR. We had to use NMR to find the signal that corresponding to the OPV property.

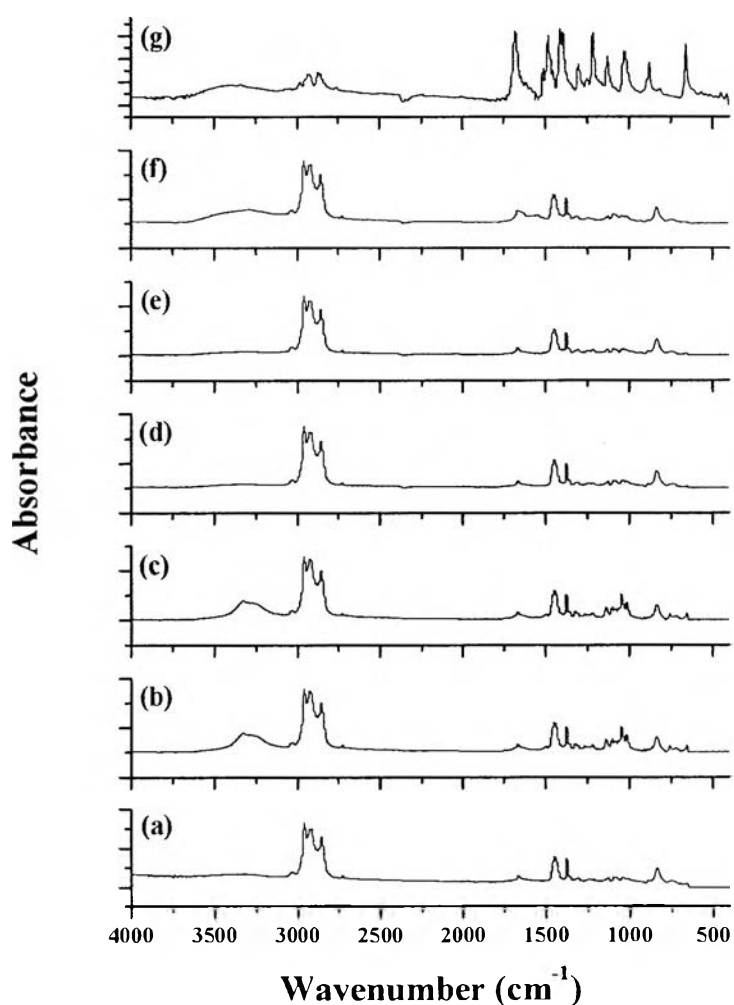


Figure 4.38 FTIR spectra subtracted by natural rubber of natural rubber grafted with OPV (a) 0%, (b) 0.5%, (c) 1 %, (d) 2%, (e) 3%, (f) 4 wt%, and (g) OPV.

The copolymer was swollen with CDCl_3 . The ^1H NMR spectrum (Appendix E) was operated on the NMR spectrometer. From the ^1H NMR spectra, the copolymer composition was determined by signal area of the specific functional group of OPV and isoprene.

The result shows signal at 7.42 (ArH+CH=CCN), 7.2 (ArH), 6.9 (ArH), 3.95 (O-CH₃), 3.87 (O-CH₂), 1.7 (CH), and 1.57-1.33 (=CH₂) ppm. They indicate that OPV groups have been bound to natural rubber (Oliveria *et al.* (2005)). The OPV molecules are easier to graft on natural rubber than PPV.

Table 4.6 The ratio of OPV grafted natural rubber calculated from signal areas of NMR spectrum

Sample	Signal area per H		Mole Ratio	
	3.95 ppm	5.2 ppm	OPV	Isoprene
3 wt%OPV	0.03	1	2.91	97.09

* 3.95 ppm is O=CH₃ (3H), 5.2 ppm is C=CH (1H)

The thermal stabilities (Figure 4.39-4.40) of NR-g-OPV samples show that the amount of OPV added in system does not affect to thermal behavior. They still behave like natural rubber and have one transition of the onset of degradation about 375°C that made them loss 98 wt%. The centers of DTG spectra still show at 375°C, when the amount of OPV increases to 4% weight.

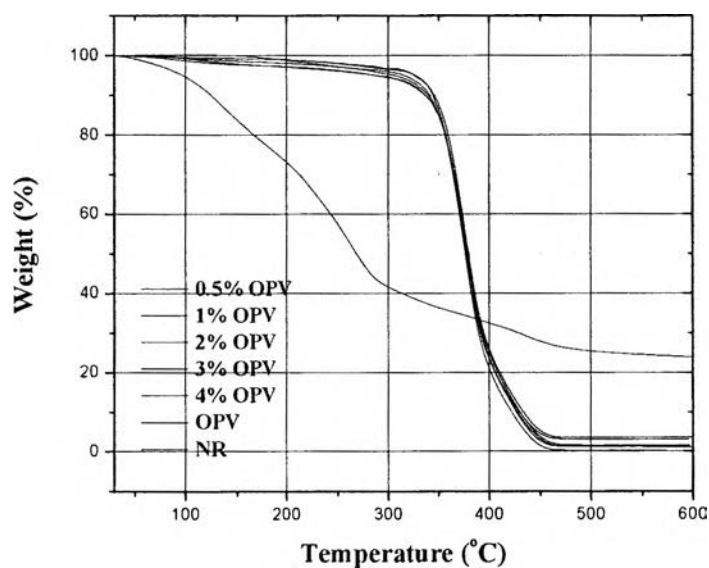


Figure 4.39 TGA thermograms of NR, NR-g-OPV 0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, and OPV.

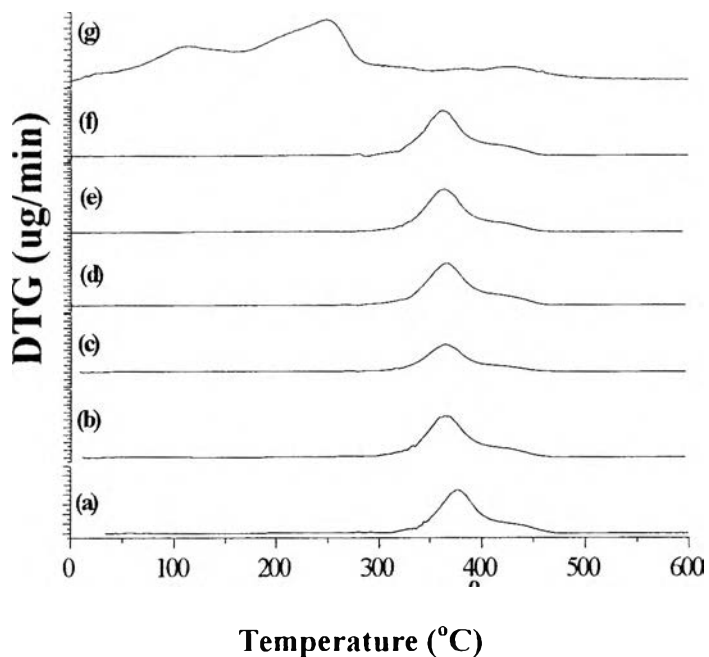


Figure 4.40 DTG spectra of natural rubber grafted with OPV (a) 0%, (b) 0.5%, (c) 1 %, (d) 2%, (e) 3%, and (f) 4 wt%, and (g) OPV powder.

From the Figure 4.41, it shows the glass transition temperature of copolymer of natural rubber-g-OPV 3 wt% is -62.6°C . The thermal properties of copolymers are changed by the amount of added OPV.

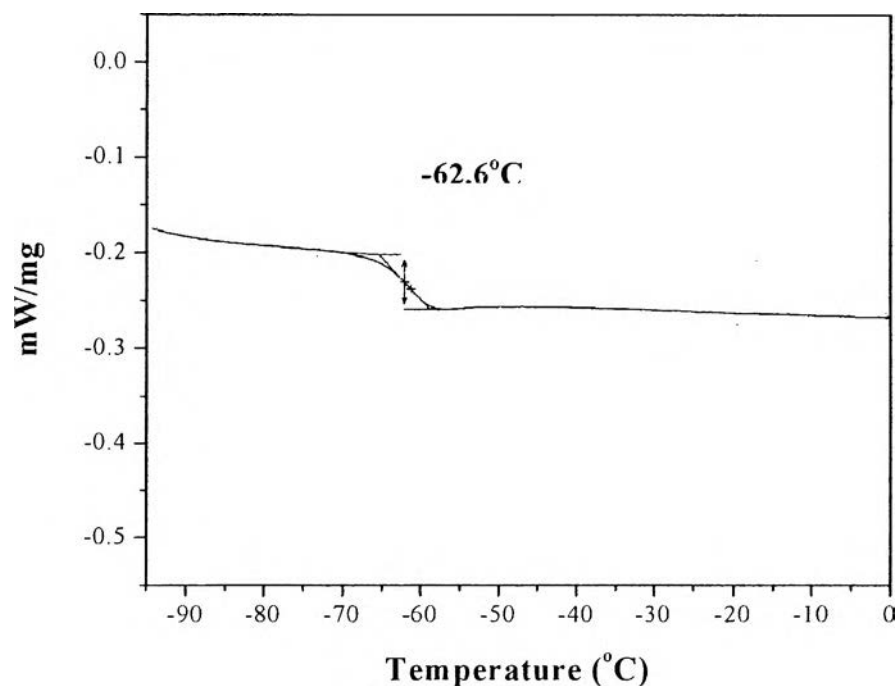


Figure 4.41 The DSC result of natural rubber grafted with OPV 3 wt%

The maximum absorption peak can be seen not only in absorption spectra but also in the excitation spectra. When photons excite the fluorescence molecules, they will absorb energy as shown in the Figures 4.42. The highest peak of natural rubber and copolymer are 450 nm and 478 nm, respectively, when they were excited by monochromatic light at 520 nm.

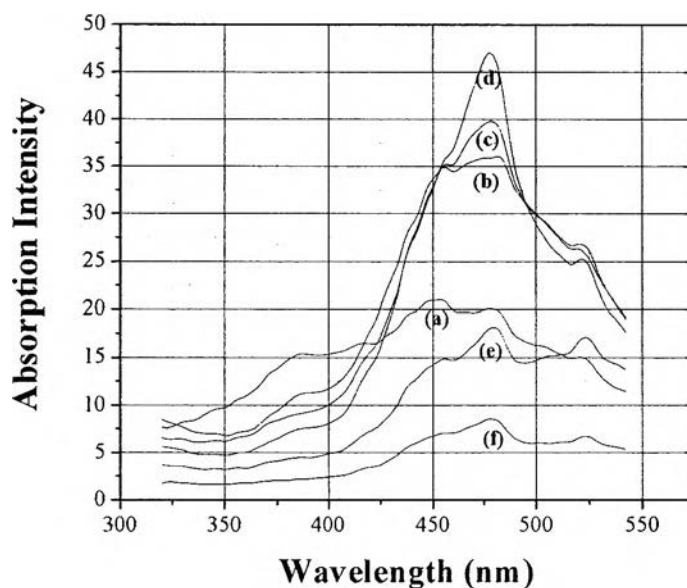


Figure 4.42 Excitation spectra of natural rubber grafted with OPV (a) 0%, (b) 0.5%, (c) 1 %, (d) 2%, (e) 3%, and (f) 4 wt%.

The photoluminescence occurs when electrons return to the electronic ground state from an excited state and lose energy as photons. The color observed depends on the lost energy. Films give broad emission with a red shift of λ_{max} to 614 nm, suggesting the presence of molecular aggregates in the excited state. The photoluminescence of copolymers changes with the amount of luminescent molecules. In Figure 4.43, the red shift occurs as a function of the dye concentration. When the molecules of OPV close to each other, both excimer formation and red shift are tentatively occurred. The red shifts are in good agreement with the reports by Crenshaw *et al.* (2003), Crenshaw *et al.* (2005), Lowe *et al.* (2002), and Pucci *et al.* (2005a).

The OPV-g-NR shows photoluminescence (after excited by 480 nm) at the range of 580-620 nm (orange to red) dependent on the amount of grafted PPV. This peak becomes red shifted with OPV content. The red shift occurred at 583, 584, 602.5, and 615.5 nm with increasing PPV content. This suggests that the conjugated length increases with OPV content (Figure 4.43).

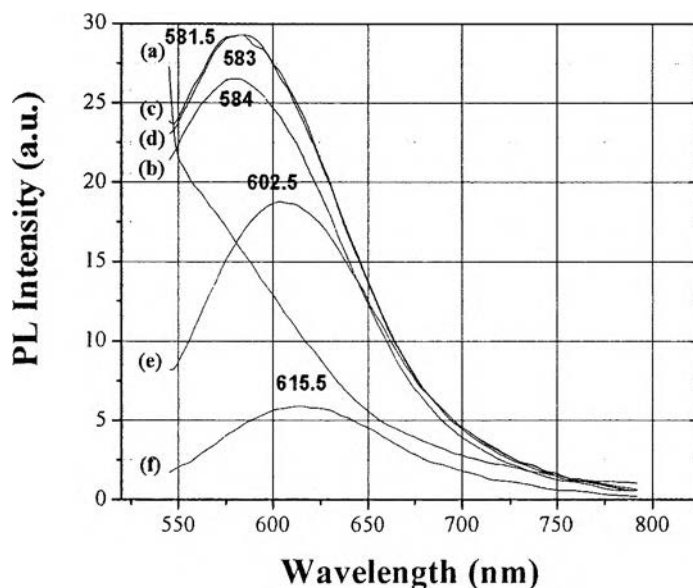


Figure 4.43 Emission spectra of natural rubber grafted with OPV (a) 0%, (b) 0.5%, (c) 1 %, (d) 2%, (e) 3%, and (f) 4 wt%.

During stretching, films show red shift behavior like the copolymers of natural rubber and PPV. These results are due to the increased conformation order to bring about aggregation of dye molecules. The percentage strains 50-200% are not adequate enough to separate the dye molecules but leads to align them to be excimer. This can be seen in natural rubber grafted with OPV 0.5 wt%, 1 wt%, and 2 wt% shown in Figures 4.44, 4.46, and 4.48, respectively.

From Figure 4.45, 4.47, and 4.49, an increase in percentage strain ranging from 0 % to 200 % results in red-shifts of the emission. For OPV 0.5 wt%, and OPV 1%wt, the critical strains induce blue shift shown at 150 % and 50% respectively. The critical strain decreases with the amount of OPV in copolymer. This caused the higher aggregation of dyes molecules, the easier become to the plastic like with increasing strain.

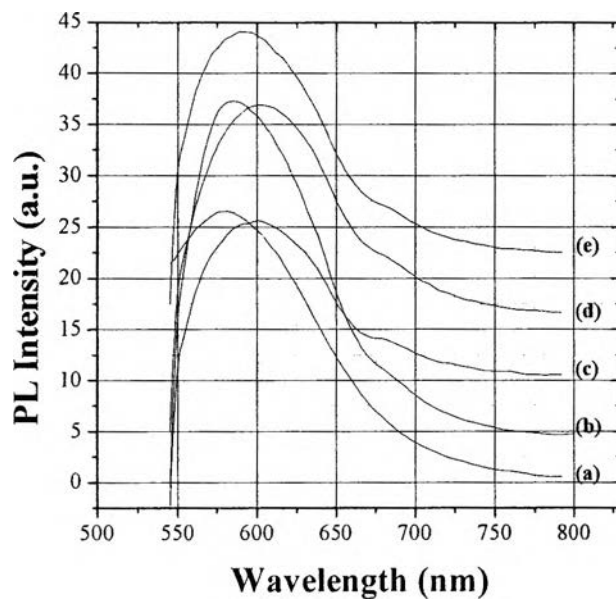


Figure 4.44 Emission spectra of natural rubber grafted with OPV 0.5 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and(e) 200%.

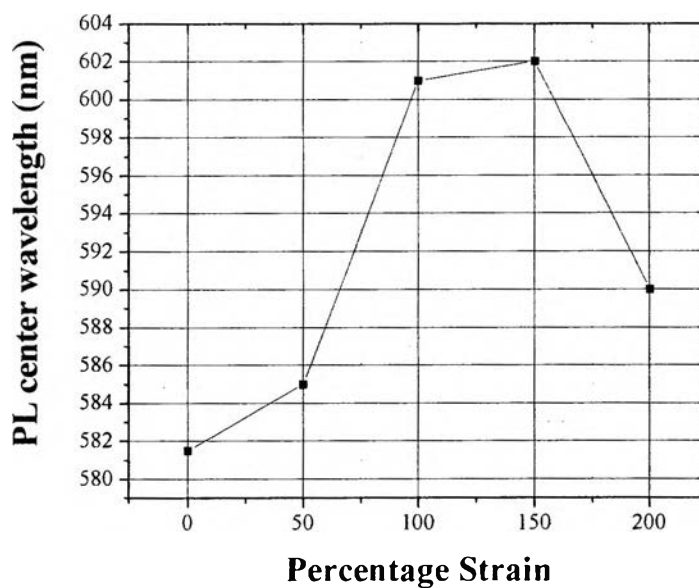


Figure 4.45 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with OPV 0.5 wt%.

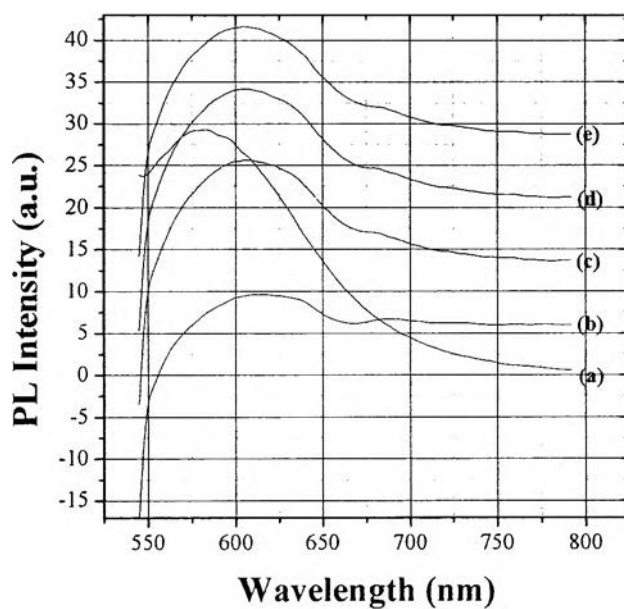


Figure 4.46 Emission spectra of natural rubber grafted with OPV 1 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and(e) 200%.

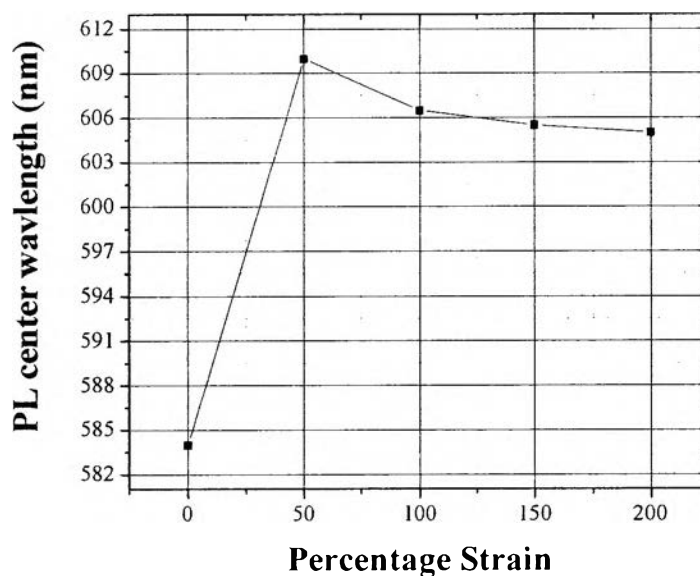


Figure 4.47 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with OPV 1 wt%.

For OPV 2 wt%, the critical strain induced blue shift is not shown. Figure 4.48 and 4.49 suggest that aggregations of dyes molecules are forced to get the longer conjugation length.

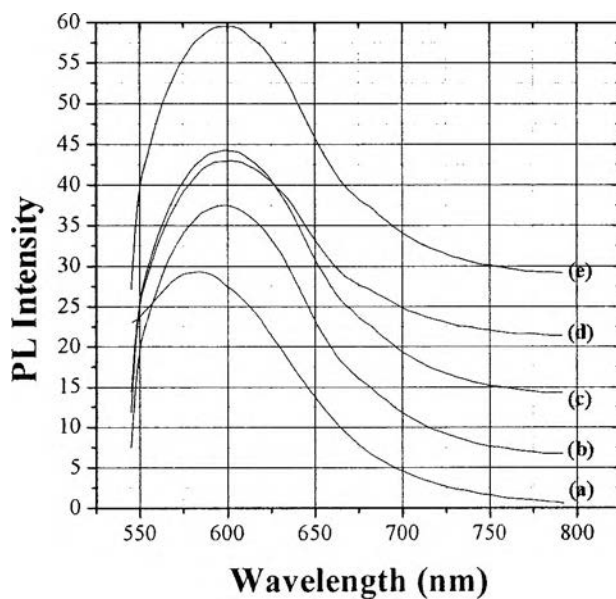


Figure 4.48 Emission spectra of natural rubber grafted with OPV 2 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and(e) 200%.

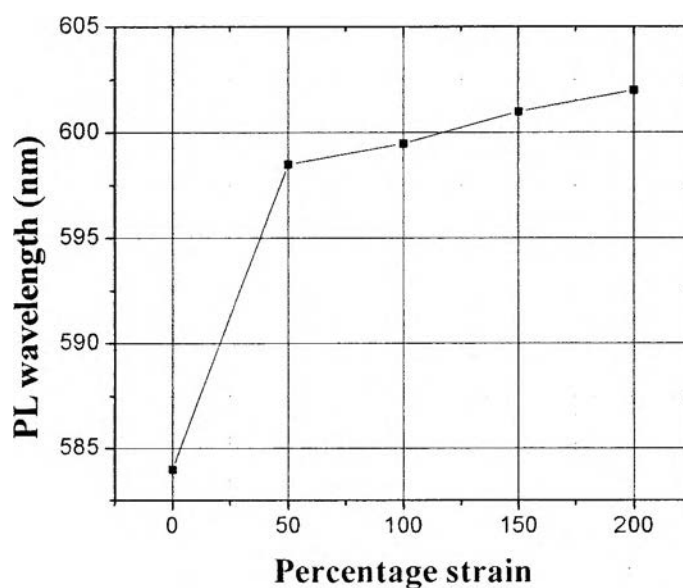


Figure 4.49 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with OPV 2 wt%.

The influences of solid-state tensile deformation on the emission characteristics of natural rubber grafted with OPV 3 wt% and 4 wt% are difference from the others (Figures 4.50 and 4.52, respectively). The emissions with increasing percentage strain were shifted to shorter wavelength. The natural rubber grafted with OPV 3 wt% (Figure 4.51) at various percentage strain 0%, 50%, 100 %, 150%, and 200% emitted light with a maximum peak at 602.5, 599, 598.5, 595, and 590.5 nm, respectively.

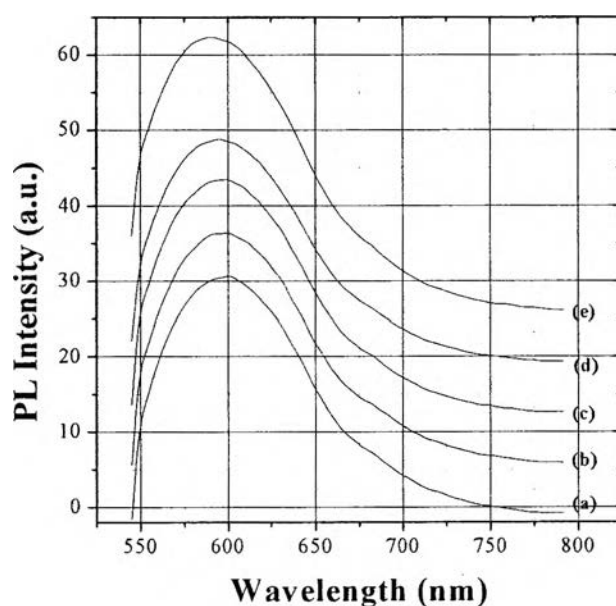


Figure 4.50 Emission spectra of natural rubber grafted with OPV 3 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and (e) 200%.

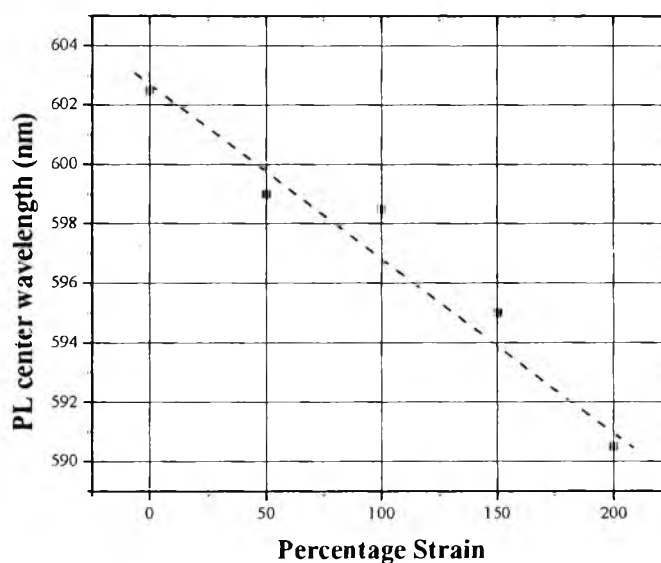


Figure 4.51 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with OPV 3 wt%.

The natural rubber grafted with OPV 4 wt% (Figure 4.52 and Figure 4.53) at various percentage strain 0%, 50%, 100 %, 150%, and 200% emitted light with a maximum peak at 615.5, 609.5, 608.5, 601, and 600 nm, respectively. Their emission changes due to the disruption of the excimers and detaching from excimers to isolated excited molecules or the conjugation length is shorten (Crenshaw *et al.* (2003), Crenshaw *et al.* (2005), Lowe *et al.* (2002), and Pucci *et al.* (2005a)).

It is clearly seen that the light emission spectrum could be tuned by not only controlling the ratios of dye content but also the percentage strain loaded on samples.

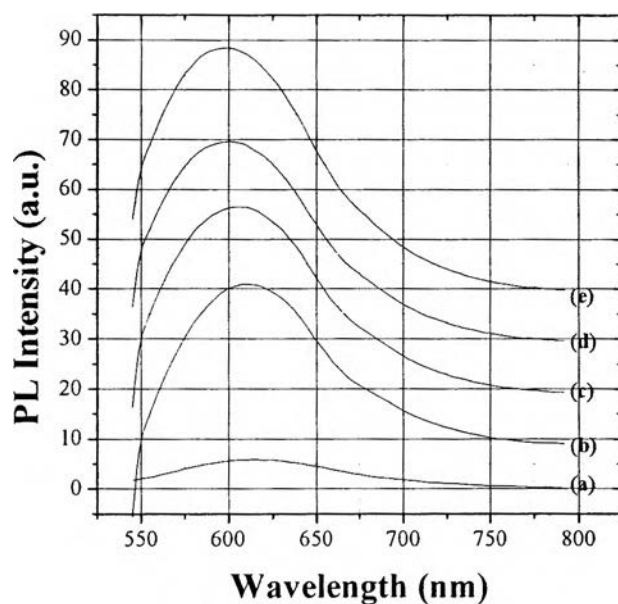


Figure 4.52 Emission spectra of natural rubber grafted with OPV 4 wt% at various percentage strain (a) 0%, (b) 50%, (c) 100 %, (d) 150%, and(e) 200%.

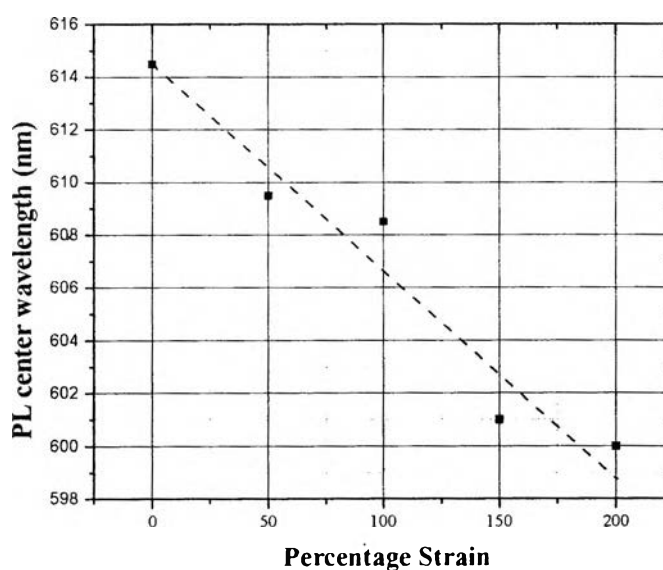


Figure 4.53 The shift of the PL center wavelength vs. percentage strain for natural rubber grafted with OPV 4 wt%.

The free radical polymerization in this study used AIBN as initiator under temperature 70°C. The molecular weight of products can be used to verify the grafting. The results in Figures 4.54 show chromatogram of OPV-g-NR. The

copolymer that has higher amount of OPV has faster elution time than another that has lower amount of OPV. This means the higher OPV grafted on natural rubber, the higher molecular weight of copolymer. This is clear that OPV could be grafted on main chain of natural polymer.

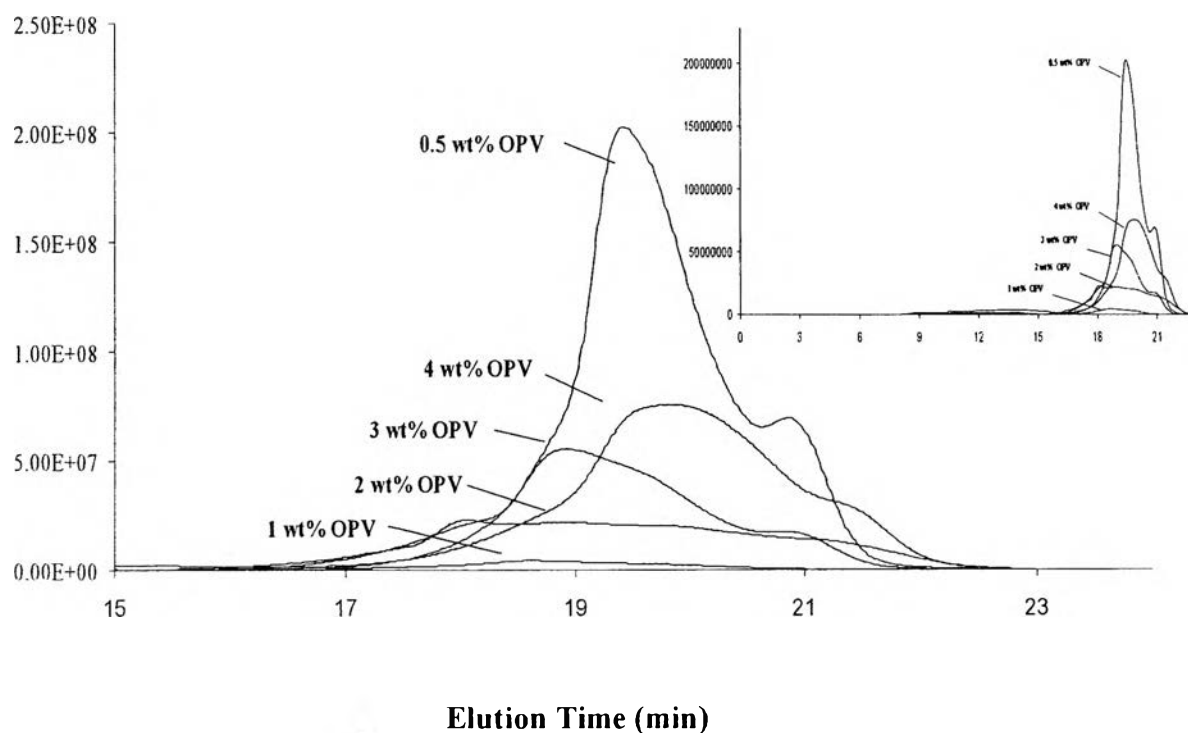


Figure 4.54 The chromatograms of OPV-g-NR copolymers.

4.5 Conclusions

In this work, PPV and OPV act as the guest molecules to graft onto the main chain of natural rubber. The PPV precursor and PPV is prepared following the Wessling routes, using α, α' xylene chloride and the preparation of OPV carried out by using 2,5-Dimethoxy terephthaldehyde and (10-dodecyloxyphenyl) acetonitrile as the raw materials. The grafting of either PPV or OPV onto natural rubber was prepared by free radical polymerization using the classic initiator, AIBN.

The results of NMR led to the calculation for the mole ratio of successful dye grafted natural rubber using signal areas of NMR spectrum of PPV: isoprene and OPV: isoprene which are 0.99:99.01 and 2.91: 97.09, respectively.

The PL emission behaviors of natural rubber filled with various concentration of either PPV or OPV between 0.5 wt% to 4 wt% show that when the concentration of PL dye is increased, the red shift increases. This suggests that the higher dye concentrations lead to the aggregation of dye molecules, excimer formation, and longer conjugation length.

The photoluminescence property of copolymers as a function of strains is observed. For PPV-g-NR with 0.5, 1, 2 wt% of PPV, the red shift is occurred at draw ratio lower than 100%. The strain could lead to aggregate the dye molecules. For the copolymers with PPV 3% and 4% by weight, they do not show the red shift along with various stretching. That means the aggregations of dye molecules are broken, even though the stress allows the chains align to high degree of linearization. During initial deformation, natural rubber filled with OPV 0.5 wt%, 1 wt%, and 2 wt% show red shift. These results are due to the increased conformation order of dye aggregation. The influences of solid-state tensile deformation on the emission characteristics of natural rubber filled with OPV 3 wt% and 4 wt% are difference from the others. The PL emissions were shifted to shorter wavelength with increasing percentage strain. Their emission change, due to the disruption of the excimers and the emission alters from excimers to isolated excited molecules. In other words, the conjugation length of the photoluminescence dyes is shortening.

We can conclude that PPV and OPV can be used to improve the photoluminescence in natural rubber. There are the possibilities to turn the emission of copolymer by stressing, and vary the concentration of the dye molecules.

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4.7 References

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