# Photoluminescence of the electron irradiated Polystyrene

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# 1. Introduction

During last few years, polymer light emitting diode (PLED) has shown impressive performances such as flexible display and single-color PELD display. So, there are a lot of efforts to synthesize the light emitting polymer at this present. However chemical synthesis method (most of light emitting polymer was synthesized by chemical method) has some defects such as complicated process and impurities. In this paper, we suggest a new light emitting polymer synthesis method using the electron irradiation with polystyrene (PS) film.

# 2. Methods and Results

#### 2.1 Experiment methods

Commercialized PS film with 25  $\mu$ m thickness (GoodFellow, ST311025) was used in the experiments. Before the electron irradiation, the PS film was rinsed with 99.9% pure ethanol and was attached on silicon substrate. And then, the polymers were irradiated with an electron beam, which was generated from a thermionic electron gun with a tungsten filament cathode. The irradiation was carried out in a vacuum chamber under a pressure of less than  $2 \cdot 10^{-5}$  Torr. The electron-beam energy was fixed at 50 keV and electron fluence was varied with the experiment time rather than the current density because of reducing the thermal variation.

In order to investigate the effects of the electron beam irradiation of the light emission properties of PS film, PL spectra was measured. PL spectra were excited using the 325nm line of the Xe lamp. UV/Vis spectroscopy measurements were performed to obtain information on the behavior of the hydrocarbons and hydrogenated aromatic units in PS film as a function of the electron irradiation process.

### 2.1 Photoluminescence

Figure 1 shows visible PL spectra for electron irradiated PS films with different electron fluence. The electron fluence was varied from  $3.5 \times 10^{15} \text{ cm}^{-2}$  to  $4.62 \times 10^{16} \text{ cm}^{-2}$ . As shown Figure 1, the pristine PS film did not show any visible PL emission. However, after the electron irradiation, PS film exhibited strong deep blue emission located around 410nm. In addition, both intensity and location of PL were changed as variation of electron fluence. At low irradiation, PL intensity increase with increasing the electron fluence but above

the critical electron fluence, PL intensity decreased with increasing the electron fluence.



Fig. 1. PL spectrum of the electron irradiated PS films.

In case of PL location, the PL spectrum was red shifted with electron irradiation.

### 2.3 UV/ Vis Spectrum

In order to investigate the origins of PL of electron irradiated PS film, UV/Vis spectroscopy was used. Figure 2 reports the absorption spectra of PS pristine and electron irradiated samples varied with electron fluence.



Fig. 2. UV/ Vis absorption spectrum of the electron irradiated PS films

There are two strong peak at 220nm and 260nm in PS pristine for the  $\pi \rightarrow \pi^*$  transitions of aromatic compounds [1]. Figure 2 also shows not only increase of a new absorption band at 230nm and increase of intensity in UV-vis region but also a shift of absorption from the UV toward the visible as increase of electron

irradiation. This effect is associated to decomposition of aromatic ring in PS pristine and formation of new bonds in the polymer chain. According to H. Kaczmark, increase of absorbance at the UV-vis region and shift the absorption spectrum caused by increase of conjugated double bond [2].

In addition, the shift in absorption edges under electron irradiation was correlated with optical gap  $E_g$  according the Tauc's expression [3].

$$E\alpha = B(E - E_g)^2$$

Where  $\alpha$  is the optical absorption coefficient and *E* is the photon energy.



Fig. 3. Variation of Tauc UV/ Vis absorption spectrum of the electron irradiated PS films

Figure 3 shows that decrease of optical gap of electron irradiated PS film with increasing electron fluence. This result was also correlated to formation of  $sp^2$  conjugated double bond in irradiated PS film, because optical gap decreases with increasing the  $sp^2$  fraction [5].

### 3. Conclusion

It is generally accepted that an electron irradiation produces both  $sp^2$  and  $sp^3$ -bonded carbon inside the polymer. In addition,  $sp^2$  carbon structures embedded in  $sp^3$  bond induce the PL and its emission energy decrease with increasing  $sp^2$  fraction or  $sp^2$  cluster size [4, 5]. According to results of UV/Vis spectroscopy,  $sp^2$ carbon structures were formed in electron irradiated PS film and its fraction was increased with electron fluence. Therefore it can be thought that  $sp^2$  carbon structures were formed by electron irradiation in PS film and PL caused by these  $sp^2$  carbon structures embedded in  $sp^3$ bond. And also PL and optical band gap energy decrease due to the increase of  $sp^2$  carbon fraction with electron irradiation.

In case of variation of PL intensity, it is suggested that below the critical electron fluence, the irradiation induces increasing the amount of  $sp^2$  carbon clusters which acts as origin of PL emission. However, above the critical fluence, electron irradiation induces the larger  $sp^2$  carbon cluster which leads to a decrease in the carrier confinement effect, so that PL intensity was decreased [6].

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