

Optical properties of proton-irradiated polymers

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1. Introduction

Recently, organic semiconducting materials have gained a broad interest due to their potential for organic electronic devices such as organic light emitting diode (OLED), organic photovoltaic devices and organic field-effect transistors (OFETs) [1]. Optical properties of organic semiconducting materials are important for practical application. For example, the power conversion efficiency of organic photovoltaic devices is mainly affected by absorption properties of organic materials. Proton irradiation is one of the efficient methods to change the optical properties of organic materials. In this paper, we investigate the changes of optical properties of various polymers using the proton irradiation.

2. Methods and Results

Energy of 1.5MeV, 200keV and current density of $1 \mu\text{A cm}^{-2}$ proton beam is used for irradiation was carried out in a vacuum. Polystyrene (PS), Poly(1-vinylnaphthalene) (P1VN), Poly-3-hexylthio phene (P3HT) poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene vinylene(MEH-PPV), Poly[9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl] end capped with 2,5-diphenyl-1,2,4-oxadiazole (ADS106) are selected as a precursor. In order to characterize the luminescent properties, photoluminescence (PL) spectroscopy is used and UV/Vis absorption spectra are measured for evaluated the optical band gap.

2.1 Polystyrene

Figure 1a and b shows fluorescent image and visible PL spectra for proton-irradiated PS films with different proton fluence. The proton energy is 1.5MeV and fluence was varied from $1.0 \times 10^{13} \text{ cm}^{-2}$ to $1.13 \times 10^{16} \text{ cm}^{-2}$. The pristine PS film did not show any visible PL emission. However, after the proton irradiation, PS film exhibited strong deep blue emission located around 410nm. In addition, both intensity and location of PL were changed as variation of proton fluence. At low irradiation, PL intensity increase with increasing the proton fluence but above the critical fluence, PL intensity decreased with increasing the proton fluence.

Figure 1c shows not only increase of absorption intensity in UV-vis region but also a shift of absorption from the UV toward the visible as increase of proton irradiation. Moreover, the optical bandgap (Tauc gap) of the irradiated sample decreased with increasing the proton dose (Fig. 1d). These phenomena suggest that

conjugated carbon units in the form of olefinic chains or aromatic rings are generated in irradiated PS and that the conjugation length increases as a function of the irradiation.[2,3] Therefore, proton irradiated PS shows semiconducting characteristic such as low band gap and luminescence.

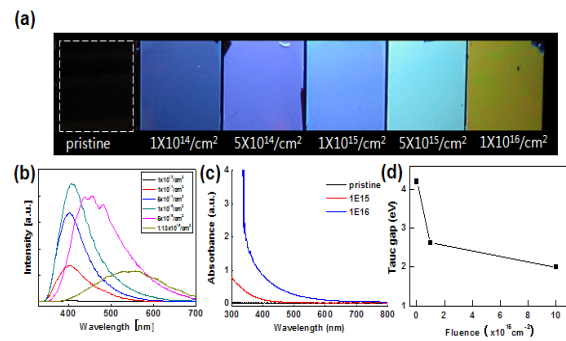


Fig. 1. Fluorescent image (a) and PL spectrum (b) of the 1.5MeV proton irradiated PS films. Absorption spectrum (c) and optical band gap (d) of the 200keV proton irradiated PS films

2.2 Conjugated polymer

MEH-PPV and P3HT are well known as a commercialized semiconducting polymer for organic photovoltaic device. ADS106 is a one of the red luminescent conjugated polymer. Figure 2a-c shows the change of absorption properties of some conjugated polymers after 200keV proton irradiation. According to the UV-vis results, differing from PS, visible light absorption of all of three conjugated polymer was reduced and blue shift, even though a little red shift was occurred at the high dose. This result shows that at the low dose proton irradiation induce chain conformational disorders and chain scission dominantly and sp^2 carbon are clusterized again at the high dose. [3]

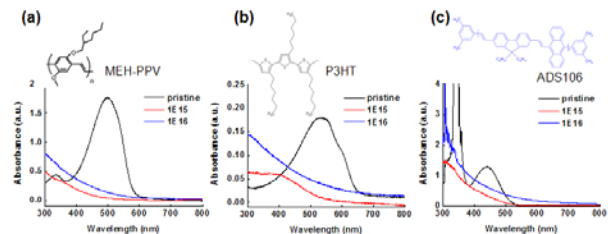


Fig. 2. Absorption spectrum of a:MEH-PPV, b:P3HT, and c: ADS106 after 200keV proton irradiation.

2.3 Poly(1-vinylnaphthalene)

P1VN is one of the polymeric hole-transport materials. Fluorescent and absorption properties of proton irradiated P1VN is similar with PS. Until critical fluence, PL intensity increase with increasing the proton fluence and red shift after irradiation. Absorption was also increased and red shifted with the fluence. Therefore, it can be concluded that clustered sp^2 conjugated double bond are induced by proton irradiation.

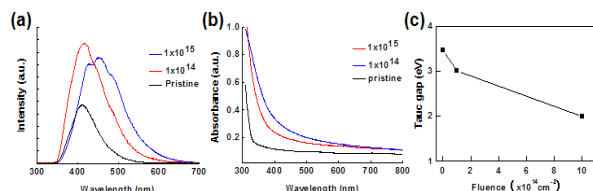


Fig. 3. PL spectrum (a), absorption spectrum (b) and optical band gap (c) of the 200keV proton irradiated P1VN films.

3. Conclusions

In this work, we were able to understand the proton irradiation effect on the various polymers. It is generally accepted that proton irradiation produces both sp^2 and sp^3 -bonded carbon inside the polymer, while the irradiation may induce both cross-linking and chain scission. In case of PS and P1VN, sp^2 carbon structures were formed dominantly, resulting in red shift of PL and absorption spectrum and increase of absorption and decrease of optical band gap. On the contrary, in case of conjugated polymer, proton irradiation induces chain conformational disorders and chain scission dominantly.

REFERENCES

- [1] Liming Dai, Derthold Winkler, Linin Dong, Lin Tong, and Albert W. H. Mau, Conjugated polymers for light-emitting applications, *Advanced materials*, Vol.13, p. 915, 2001.
- [2] M. Füle, S. Tóth, M. Veres, I. Pócsik, M. Koós, Two bands structure of the photoluminescence excitation spectrum of the composite bands in a-C:H luminescence, *Diam. Relat. Mater.* Vol.14, p.1041, 2005.
- [3] K. W. Lee, K. H. Mo, J. W. Jang, and C. E. Lee, Proton-irradiation effect on the luminescence of the MEH-PPVconjugated polymer, *Solid State Communications* Vol.141, p.57, 2007.