

Fabrication of organic luminescent materials by electron irradiation

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1. Introduction

Nowadays, the luminescent materials with conjugated structures are because of their low cost, easy manufacturing and chemical, physical characteristic features, giving great uses in various fields such sensors, displays, and solar cells [1]. Though these conjugated materials, polydiynoic acid (PDA) is easily changed from red and blue with change of photoluminescence property, many researches are going for luminescence and sensor [2].

We polymerized PCDA newly with electron beam irradiation, which induce not only side chain change but also conjugation structure change [3]. So we can get new chemical, physical property that cannot be found by other polymerization and plus, we can adjust degree of change as irradiation dose.

By electron beam irradiation to PCDA newly, we induce irradiation character change and analyzed it by Photoluminescence, FT-IR, FT-Raman.

2. Methods and Results

2.1 Methodology

2.1.1. Equipment

We employed irradiation equipment using thermo electron emission. We send an electric current on Ta filament to heat and generate thermo electrons and then give a 50kV to accelerate and irradiate those thermo electrons. And we measured Photoluminescence at 532nm and FT-Raman at 1064nm of excitation condition each

2.1.2. Procedure

Adding 15 %(mass ratio) PCDA to CH_2Cl solution and dissolve using sonicator. Filter that through 450nm filter. After cleaning 1cmx1cm Si plate by Ethanol and distilled water, dry it using Air gun. Drop cast 10 μl of solution on center of plate for FT-IR and FT-Raman spectroscopy and 20 μl of solution for PL spectroscopy. Each of them is operated at the normal temperature followed by safekeeping in vacuum condition to intercept a polymerization by UV in air.

Place two different types of plates to beam region of 2.5cm diameter on irradiation plate and fix them using Ag paste. Send an electric current of 50kV, 10mA at the vacuum condition maintaining the temperature of plate for 288K. Irradiation times are controlled to 1, 7, 15, 40, 50, 60, 120, 180mins.

2.2 Result

2.1.1 Sample images

The blue pristine was originally white. This change is caused by UV in air. Compared to heat, electron beam lets sample to become a black one at 1, 7, 15 minutes before red phase. This black state is partially shown at 50, 60 minutes. After that, this becomes yellow one at 120, 180 minutes. We can assume that mixed color of red and yellow is shown at 50 min. and also red and black at 50, 60 minutes.

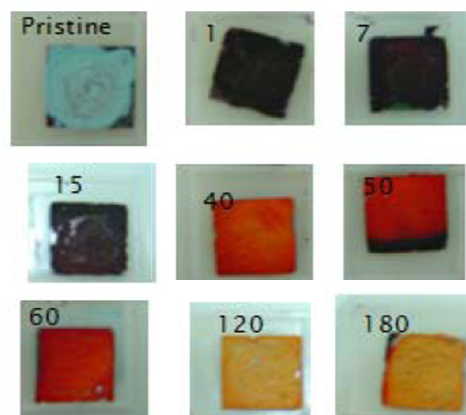


Fig. 1. Sample images as irradiation time. It changes from white/blue to black, red and yellow.

2.1.2 Photoluminescence (PL)

The photoluminescence (PL) is correlated to with polymer's illuminating characteristics. We excited at 532nm and then observed the result that shows transition through various minutes. Sample of 0 min shows two peaks at 408nm and 520nm. After that, there was no peak for 1, 7, 15mins having black phase that absorb most of lights.

Sample for 40min. shows a big peak at 611nm and peaks become extremely small for 50, 60 minute. Moving to long wave, 660nm. 120, 180 minute. Shows bigger peaks at 577nm, 582nm.

40, 120, 180mins showing good illuminating status have yellow light, and the differences of PL peak among 40, 120, 180mins. peak is caused by changes of conjugation lengths by electron beam irradiation.

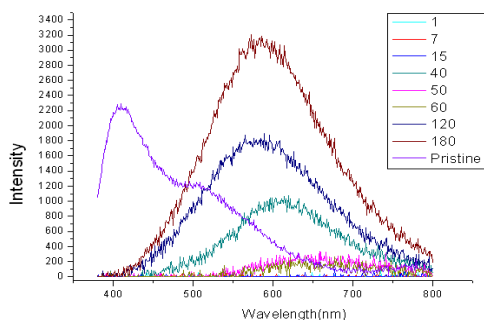


Fig. 2. Photoluminescence change as irradiation time. There is high peak at 40minutes, 120 minute and 180 minute.

2.1.3 FT-IR

FT-IR analysis shows that there were changes of CH₂ symmetric bond and asymmetric bond peaks. According to graph below, variation aspects of each peak's intensity and wavenumber are consistent. First, it can be seen from left graph that each peaks have intensity decrease till 50 min. with similarity. It says that sample becomes more irregular by rotation of CH₂ structure of side chain by irradiation to regular blue phase on second dimension. Both symmetric and asymmetric have similar variation patterns including blue shift to higher wave number till 50 min. that means more irregular structure. After 50 min., there exists 2 new phases that we can find trough peak changes [4].

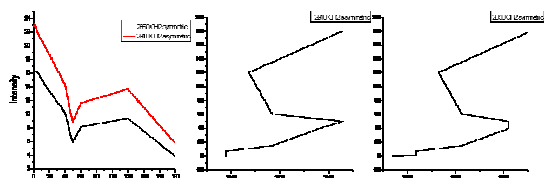


Fig. 3. Intensity and wavenumber of 2850(symmetrical) and 2918(asymmetrical) CH₂ Bond.

2.1.4 FT-Raman

FT-Raman result can let us to know about intensities and peak shifts of C=C and C≡C bonds.

Variation of intensity shows that both double and triple bond as conjugation structure were pretty big just after 1 min. and then sharply decreased at 7 min. till 40 min. After that, they increased. As EB irradiation period getting longer, CH₂ group rotates that causes more irregular and less conjugation intensity.

Also, wavenumber of double bond shows that backbone originally irregular at monomer state becomes regular one at 1 min. followed by disordered state again. Triple bond didn't show any decrease of wavenumber, but it had some similar aspect of change with double bond, that is, arise of new phase after 40 min. This blue shift of wavenumber says that regular form at 1 min. followed by more irregular form meaning declined conjugation length [5].

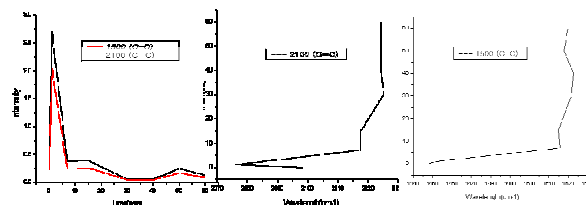


Fig. 4. Intensity and wavenumber of 1500 (C=C) and 2100 (C≡C) Carbon bonds.

3. Conclusions

At first the monomer PCDA becomes a blue-red middle stage of purple phase (1, 7, 15 minute.) by rotation of side chain that causes irregular form. After that, interactions among PCDA chains are weakened and conjugation is changed that goes to red phase at 40 minute with yellow-red color mixed visible aspect. Hereafter, side chain rotates again as a purple phase that shows smaller PL as well as red and black mixed visible aspect at longer wavelength. And then, there arises a change of conjugation that has a peak around 560nm according to red phase.

This shows that backbone consists of carbons are maintained and there arises side chain mutations totally different from that of red phase. And as we increase irradiation, there is unknown and very different 'yellow phase' appeared. Its color is different and it shows 580nm peak and its almost same as sobuilized red phase PCDA. So we can assume that it is due to cut of long polymer chain to short one caused by long term EB irradiation.

These samples are showing huge different PL and absorption at each stage. So we can make it as various kinds of sensors. And Black phase's huge absorption can be considered as solar cell material. Plus, we can get huge intensity and different colors only by irradiation; we can use this material as survey of irradiation effect of polymer, especially side chain. By these things, we can conclude that the material change of electron beam irradiation is very different from other method and it deserves to research.

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