

Short Communication

Photoluminescence properties of PADC Irradiated with Ultraviolet Radiation of Short Wavelength (UVC)

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This study sought to investigate photoluminescence (PL) emission spectra of poly allyl diglycol carbonate (PADC) irradiated with short wavelength ultraviolet radiation of 254 nm. PADC samples were irradiated with UVC of 254 nm from UVC Corsslinker (Hoefer) with different doses ranging from 900 J/cm² to 180000 J/cm². The photoluminescence spectra of UV-irradiated PADC were measured with the aid of a spectrofluorometer (FluoroMax-4). The results revealed that the UVC of 254 nm induced modifications in the photoluminescence emission spectra of PADC. While the PL peak position shows insignificant changes, FWHM of PL increased from 9.92 eV of pristine PADC to 11.17 eV of PADC exposed to UVC dose of 900 J/cm², thereafter no significant changes were observed, irrespective the UVC dose. The photoluminescence peak intensity as well as the integrated photoluminescence intensity increases when there is an increase in the UVC doses and they are linearly correlated with UVC dose. These new findings indicate that it is possible to use photoluminescence emission spectra of PADC in dosimetric applications for ultraviolet radiation of short wavelength over a wide range of doses.

Keywords: Poly allyl diglycol carbonate (PADC); Photoluminescence; Ultraviolet radiation; Photodegradation

1. INTRODUCTION

The plastic poly allyl diglycol carbonate (PADC), that is created by the polymerization of diethylene glycol bis(allyl carbonate) (CAS No. 99567-48-9), is an optically transparent thermoset polymer [1]. In spite of PADC being originally developed and manufactured for use in optical components such as lenses, PADC is one of the most common solid state nuclear track detectors that is used in radiation detection and dosimetry, particularly for heavy ions. It is commercially known as CR-

39 detector [2-4]. Applications for PADC include up-to-date x-ray reflectivity, soft x-ray image detectors, alpha particle autoradiography, neutron and alpha radiography, charged particle spectroscopy, astrophysics, nuclear physics, radon-emanation detection, micro and sub-micro-filters production, in low linear energy transfer radiation dosimetry, and eyeglasses [2,5-12].

The monomer, which is shown in Figure 1 [1], contains three functional groups; these are: Allyl group ($\text{CH}_2=\text{CH}-\text{CH}_2-$), ether group ($-\text{CH}_2-\text{O}-\text{CH}_2-$), and carbonyl group ($\text{C}=\text{O}$). The presence of two Allyl groups leads to both the polymerization of PADC's monomers and a cross-link which results in a thermoset plastic characterized as being hard, infusible and insoluble in all solvents at room temperature.

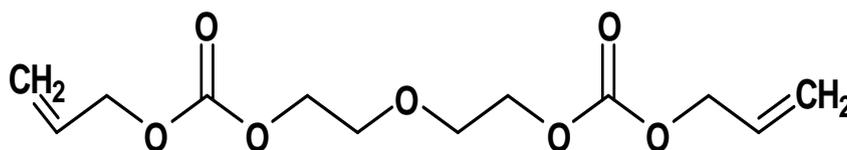


Figure 1. Repeating unit of PADC monomer.

It is a well-established fact that PADC can be degraded by low linear energy transfer (LLET) radiation such as X-and gamma rays and ultraviolet radiation, which was intensively investigated in many studies [13-16]. Ultraviolet radiation promotes chemical modifications in PADC via chain scission and photo oxidation, which becomes irreversible as alternations occur in macroscopic and microscopic properties. These induced modifications form the premise to utilize the PADC in ultraviolet radiation dosimetry [17-19]. In principle, ultraviolet radiation induced-modifications can be observed by measuring the net change in the bulk etch rate [19-20], track etch response [21], UV-Vis spectrophotometer, or by FTIR spectroscopy [17-18]. In principle, the photodegradation of PADC by ultraviolet radiation is strongly dependent on the ultraviolet radiation wavelength as highlighted by Tse et al. [17]. While UVA caused no chemical modifications as most UVA photons are not absorbed by PADC, it is found that ultraviolet radiation exposures of short wavelengths significantly changes the properties of PADC through photo-oxidation and different processes, which rely on the UV wavelength.

Recently, photoluminescence (PL) spectroscopy of irradiated solid state nuclear track detectors has gained much attention in the field of radiation dosimetry [22]. Photoluminescence spectroscopy is characterized by low limits of detection, several orders of magnitude lower than those of the most common spectroscopy techniques such as UV-Vis and FTIR spectroscopy. Consequently, it was used successfully to detect the response of PADC to gamma ray [23]. Unfortunately, the studies on the photoluminescence emission of PADC irradiated with ultraviolet radiation are insufficient and demand further investigation since understanding of the correlation between photoluminescence emission spectra and ultraviolet radiation dose may help in extending the dosimetric applications of PADC to ultraviolet radiation.

The focus of the present study is to investigate the photoluminescence emission spectra of PADC irradiated with different doses of ultraviolet radiation of 254 nm. The emphasis will be on the ultraviolet radiation of short wavelength of 254 nm dependent photoluminescence measurements. Additionally, the study will examine the use of photoluminescence emission spectra of PADC in ultraviolet dosimetric applications by measuring the integrated intensity, peak position, FWHM and peak intensity of PL band as a function of UVC doses.

2. METHODOLOGY

2.1. Materials

Poly allyl diglycol carbonate (PADC) sheets manufactured by TASTRAK (Track Analysis System Ltd., UK), with a density of 1.3 and a molecular composition ($C_{12}H_{18}O_7$) of a thickness of 1000 μm were cut into pieces of 4 cm^2 with the aid of a laser beam [24].

2.1. Irradiation

PADC samples were exposed to different doses of ultraviolet radiation of short wavelength of 254 nm (UVC) in air at room temperature in an ultraviolet radiation Crosslinker (Hoefer, UVC 5000 Ultraviolet Crosslinker) [25]. This UV Crosslinker is capable of producing variable doses of ultraviolet radiation up to 999.9 mJ/cm^2 .

2.3. Measurements

The photoluminescence spectra were measured with a FluoroMax-4 spectrofluorometer (Horiba) [26]. Excitation wavelengths were emitted from a high-pressure xenon lamp dispersed by a grating monochromator. The Florescent light is detected by a photomultiplier through a second grating monochromator. To avoid the saturation spectrometer detector, the slits of the excitation wavelength and emission wavelength are adjusted to 0.5 nm and the lack of fluorescence emission intensity was compensated by increasing the integration time of the detector to 0.5 seconds. The PADC was adjusted with an angle of 30° relative to the excitation wavelength to minimize the first and second order of diffraction. All samples were excited using a wavelength of 350 nm (3.54 eV) and the emission spectra were measured within a step of 1 nm in the range 350-to-650 nm. All measurements were performed at a constant temperature of 25 $^\circ\text{C}$.

3. RESULTS AND DISCUSSION

Upon exposure to ultraviolet radiation of short wavelength UVC of 254 nm, a discoloration of the PADC was observed as it changed to yellow. The change in the color of the PADC increased with

the increase of the UVC dose. However, this discoloration indicates the PADC has been degraded under effect of UVC, due to many concurrent chemical processes taking place in PADC which results in several different modes of damage [17]. Ultraviolet radiation of short wavelength (UVC) of 254 nm has enough energy of 4.88 eV to cleave the bonds in PADC chains with the production of free radicals [18], which initiates further complex reaction to molecular oxygen. The photodegradation will give rise to modifications in the electrochemical and optical properties of PADC. The photoluminescence of a UVC irradiated PADC sample is located between the first order diffraction at 3.54 eV (350 nm) and the second order diffraction at 1.77 nm (700 nm) of the excitation monochromator grating, both diffraction orders are minimized by positioning the PACD at an angle of 30° relative to the excitation light. Photoluminescence spectra shown in the Figure 2, which occurred between first and second order diffractions, revealed the influence of various dose of ultraviolet radiation of 254 nm on the photoluminescence emission of PADC, which was excited with 350 nm.

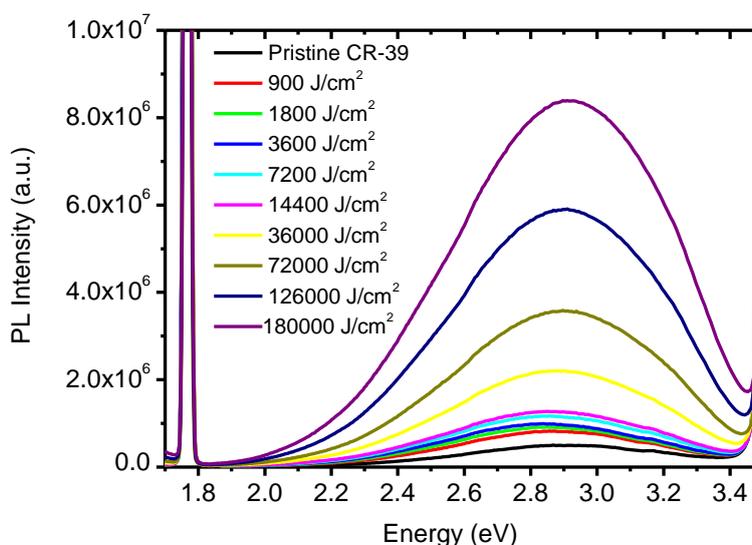


Figure 2. Photoluminescence spectra of a pristine and UVC-irradiated PADC with different doses. The excitation wavelength was 350 nm.

The reported results are similar to the results obtained by Diepens et al. [27] on bisphenol A polycarbonate (BPA-PC), which show an increase in photoluminescence intensity as the exposure time to ultraviolet radiation is increased.

From figure 2 the following characteristics relating to the photoluminescence emission spectra of UVC irradiated PADC can be deduced; these are: (1) the photoluminescence emission spectra intensity increases with the increase of the UVC dose; (2) the photoluminescence emission spectra peak position shows insignificant change in either the red or blue shift, regardless of the UVC dose. It is not an easy task to determine the aspect of the UVC interaction with PADC that is responsible for these modifications in the photoluminescence. This is simply because two main processes are taking place in PADC. In the initial stage, bonds scission in the backbone of PADC occurs which causes photo-dissociation, which in turn facilitates the formation of radicals. For higher UVC dose, cross

linking occurs due to the fact that free radicals migrate and recombine with other radicals or the main chain. Cross linking results in the formation of molecules of higher weight which may undergo irradiative recombination upon excitation with a wavelength of 350 nm. The photoluminescence emission spectra can be characterized through four parameters, which include integrated intensity, peak position, FWHM, and peak intensity, which are summarized in Table 1.

The results show a significant increase in the width of the photoluminescence spectrum from 9.92 eV for un-irradiated PADC to 11.17 eV for PADC exposed to 900 J/cm². For higher doses, no significant changes were observed. The broadening of the PL FWHM suggests that the occurrence of intra- and inter-chain energy transfer processes towards chromophores with the largest effective conjugation length produces the lowest HOMO-LUMO energy gaps. Two distinct mechanisms contribute to the broadening of the photoluminescence spectra of UVC-irradiated PADC: they are the production of new compounds as a result of photodegradation by UVC, and the increase in CR-39 surface roughness.

Table 1. Parameters of the photoluminescence emission spectra PADC irradiated with different doses of UVC of 254 nm.

UVC Dose (J/cm ²)	Integrated intensity	Peak Position (eV)	FWHM (eV)	Peak Intensity (CPS)
0	0.60E8	2.88	9.92	0.50E6
900	0.98E8	2.87	11.17	0.82E6
1800	1.11E8	2.85	10.88	0.92E6
3600	1.23E8	2.84	10.67	1.00E6
7200	1.44E8	2.86	10.60	1.17E6
14400	1.59E8	2.85	10.51	1.27E6
36000	2.72E8	2.88	10.69	2.20E6
72000	4.39E8	2.90	10.78	3.58E6
126000	7.37E8	2.91	10.51	5.91E6
180000	10.66E8	2.91	10.33	8.39E6

Figure 2 also showed the increase in the integrated photoluminescence which suggests the nonradiative recombination rate is enhanced in comparison to the irradiative one. Such an enhancement can be attributed to one of the following mechanisms: an increase in the surface density states, or an increase in surface roughness of PADC.

Figure 3 shows the dependence of the PL peak intensity of UVC-irradiated PADC on the UVC dose of 254 nm, the PADC was excited with wavelength of 350 nm. The results reveal that PL peak intensity increases linearly with the increase in the UVC of 254nm dose. This increase, however, is attributed to the new photochemical compounds formed by photodegradation of PADC under the exposure of UVC of 254 nm, which was subjected to irradiative recombination. The data in figure 3 are fitted with the following linear equation;

$$P(D) = a_1 + b_1 \times D \quad (1)$$

where D is the UVC dose measured in (J/cm^2) a_1 and b_1 are fitting parameters and amount to (727190 ± 54843) and (150677 ± 2661), respectively. From the calibration curve, b_1 which is the gradient of the straight line represents the sensitivity of PADC to UVC of 254 nm, it amounts to (150677 ± 2661) $\text{CPS}/(\text{J}/\text{cm}^2)$. However, this sensitivity is higher than those achieved by UV-Vis spectrophotometer, which pointed out by Tse et al. [17-18].

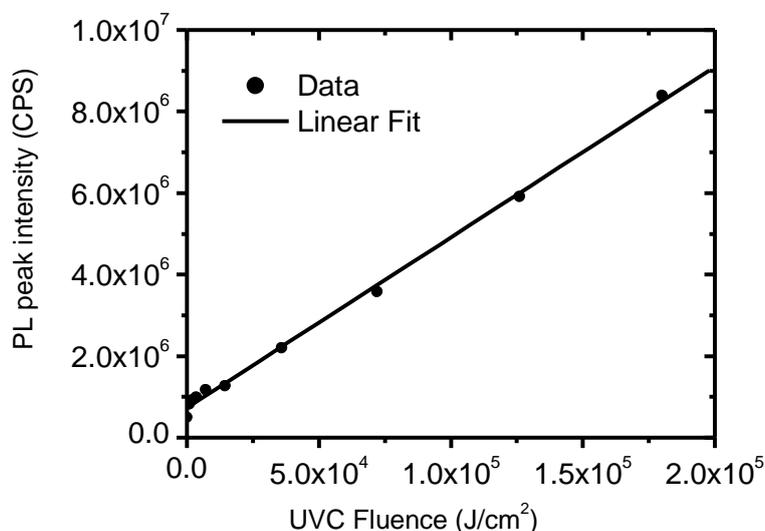


Figure 3. Dependence of photoluminescence peak intensity of PADC on the UVC dose, the excitation wavelength is 350 nm. Solid line indicates linear fitting of the experimental data with Eq.1.

The integrated photoluminescence intensity as a function of UVC dose is shown in Figure 3. The photoluminescence intensity was found to increase appreciably with UVC dose indicating positive UVC effect. The linear increase of photoluminescence intensity may be attributed to formation of irradiative recombinations of compounds formed either by scission of the functional groups such as C–C, C–H and C–O, in addition to OH and OOH formation upon irradiation with UVC [18]. The data are fitted using the following linear equation;

$$A(D) = a_2 + b_2 \times D \quad (2)$$

D is the UVC dose measured in J/cm^2 . Both a_2 and b_2 are the fitting parameters; they amount to ($8.65594\text{E}7 \pm 1.18157\text{E}7$) and (5305 ± 159), respectively. The parameter b_2 is a calibration factor between integrated photoluminescence intensity and UVC dose. The linear relationship between integrated PL intensity and UVC dose, which is valid for dose from 900 to 180000 J/cm^2 , indicates the advantage of fluorescence spectroscopy over the UV-Vis spectrophotometry which shows rapid saturation. When compared to other dosimetric techniques, which were used in ultraviolet radiation dosimetry using PADC [18, 28], the UVC dosimetry obtained from measuring fluorescence spectroscopy offers a better linear relationship.

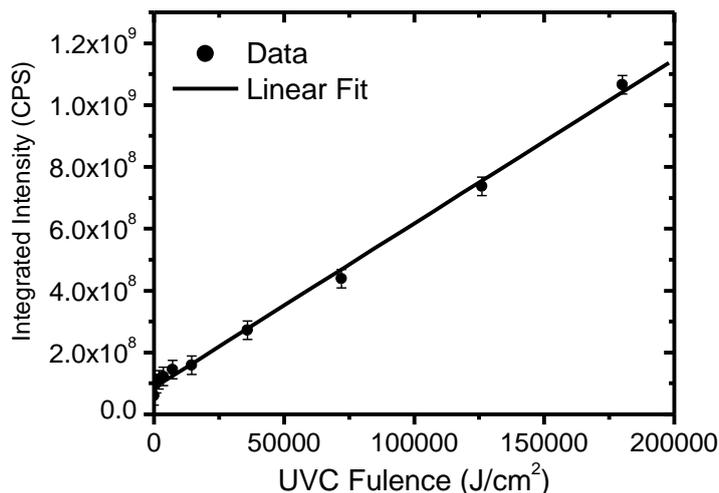


Figure 4. Integrated photoluminescence intensity dependence on the dose of ultraviolet radiation of 254 nm of PADC, the excitation wavelength is 350 nm. Solid line is a linear fit to the experimental data with Eq.2.

4. CONCLUSIONS

Throughout this paper, we have investigated the effects of short wavelength ultraviolet radiation of 254 nm dose on the photoluminescence intensity of PADC. The photoluminescence emission of PADC exhibits a strong dependence on the dose of UVC of 254 nm. The results revealed that the UVC induced modifications to the photoluminescence emission spectra of PADC upon exposure to short wavelength ultraviolet radiation of 254 nm. While the PL peak position shows insignificant changes, FWHM of PL increases from 9.92 eV of pristine PADC to 11.17 eV of PADC exposed to UVC dose of 900 J/cm², thereafter no significant changes were observed irrespective of the UVC dose. The photoluminescence peak intensity as well as the integrated photoluminescence intensity increases linearly with the UVC doses. The current findings are recommended to maximize the use of photoluminescence emission spectra of PADC in high UV dose measurements.

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