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Effect of Low Gamma-Irradiated dose on the Structure of Cellulose Triacetate Films: II. Positron Annihilation Spectroscopy

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Abstract Positron annihilation spectroscopy, thermogravimetric and FT-IR techniques are used to study the effect of low doses of gamma irradiation on microscopic structure of cellulose triacetate films. The irradiation is done at room temperature with doses ranging from 5 to 25 kGy. The ortho-positronium lifetime component associated with the pick-off annihilation of positronium trapped by the free volume is analyzed. Alternation in the ortho-positronium lifetime is observed reaching to a minimum value at10 kGy which is followed by a sharp increase at 15 kGy. Afterward, the ortho-positronium lifetime remains almost constant up to 25 kGy. The intensity of ortho-positronium component, I_3, revealed an opposite trend with respect to the ortho-positronium lifetime manner. The obtained results are discussed on the basis of free volume model. The thermogravimetric and FT-IR measurements bearded out the findings of positron annihilation spectroscopy and explained the variations on the CTA microstructure due to the effect of the low doses of gamma irradiation.

Keywords Positron annihilation, Gamma irradiation, Cellulose triacetate

1. Introduction

Materials that have two refractive indices are known as optical birefringent materials. Birefringence is one of the most important properties of polymer films that are used as wave retarders [1]. Birefringent polymers are used in modern high-performance 3D display devices and in organic electro-luminescence displays that require retarders with well-controlled birefringence and wavelength dispersion [2, 3]. Polymer such as cellulose triacetate (CTA) is typically a dielectric with Fermi energy is about 160 times as great as the thermal energy at room temperature [4]. CTA as a uniaxial material has many diverse scientific and technological applications [5] due to its attractive properties [1, 6-10]. Many of optoelectronics devices depend basically on the birefringence property of the used materials [11].

The variation in birefringence dispersion versus irradiation dose was investigated [12] leading to negative birefringence that could be utilized in CTA to design high-performance quarter wave retarders. The sign and wavelength dispersion of birefringence in CTA can be also controlled by irradiation [13]. Study the structure of irradiated polymeric materials is essential in order to produce achromatic or apochromatic retarders which can provide constant phase retardation independent of wavelength of light [14, 15]. Such retarders with white light sources are ideal for polarization spectroscopy, magneto-optical experiments, ellipsometry, polarimetry and telecommunications [16, 17].

Recently, the structure and properties of nonirradiated CTA and other types of polymers have been studied using positron annihilation lifetime spectroscopy under different preparation processes and treatments [18-28]. Therefore in this work, positron annihilation lifetime spectroscopy (PALS) is used to study the structure of CTA films subjected to γ–irradiation. Fourier transformation infrared spectroscopy and thermal analysis are applied to provide information on the structure of γ–irradiated CTA films and their induced birefringence.

2. Experimental Details

Cellulose triacetate is made from cellulose by heterogeneous acetylation of the corresponding respective cellooligosaccharide and is purified by recrystallization twice from ethylacetate – hexane. All six OH groups in the cellobiose units of cellulose are substituted by six $COOCH_3$ groups. It is usually a rigid amorphous polymer as assumed from the molecular structure (Fig. 1). Developed Fortpan photographic film plates with dimensions of 6.3 cm× 8.8 cm and a thickness of 180 ± 1 μm were investigated. The samples were irradiated with the following doses: 5, 10, 15, 20 and 25 kGy. Irradiation process with gamma rays was

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performed at the National Center for Radiation Research and Technology, Cairo, Egypt. The gamma irradiation was done using Russian cell (60Co source) of the model ISSLEDOVATEL. The dose rate of the cell was 10 kGy/100 min.

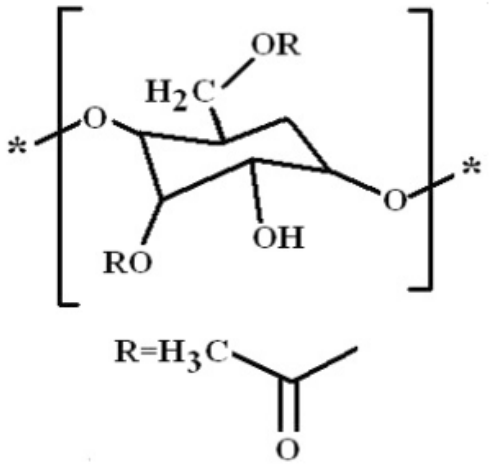


Figure 1. Cellulose triacetate chemical structure

Kinetics study of thermal decomposition was done using thermogravimetric (TGA) technique. The technique measures the change in weight of a sample during heating. It provides information on the initiation and termination of weight change. TGA gives the ability to find out the temperature (T_0) at which the thermal decomposition starts. It also allows measurements of the activation energy of thermal decomposition (E_a), which are useful for studying the thermal stability of the materials. The method is proposed by Horowitz and Metzger [29] and it has been used in the present study for measuring the activation energies of thermal decomposition. TGA is performed for irradiated and nonirradiated CTA samples in a temperature range from 20℃ up to 700℃ with a heating rate of 10℃ min.

The source employed in the positron annihilation experiments was ^{22}Na, which decays to ^{22}Ne with the simultaneous emission of positron and a γ-ray of 1.28 MeV. The positron source was prepared by drying a droplet of ^{22}NaCl aqueous solution (about 20μCi) on a thin kapton foil of 7μm thickness and 10 × 10 mm^2 area. After drying the ^{22}NaCl spot, it is covered by another similar foil using epoxy glue and evacuated for a long time (more than 24 h). The source absorption by the kapton foil is about 10% and contributed to the short lifetime components. The source was sandwiched between two identical CTA samples of about 10×10×0.7 mm^3. The positron annihilation lifetime (PAL) spectra were determined by detecting the prompt γ-ray (1.28 MeV) that accompanies the emission of a positron from the ^{22}Na radioisotope and the annihilation γ-rays (0:511 MeV). A fast–fast coincidence system with a time resolution of 250 ps was used to record all the PAL spectra. The analysis of the positron annihilation lifetime spectra was performed using the PATFIT program [30] which provides the average of lifetimes and their intensities.

Infrared vibrational absorption measurements were recorded for the present CTA films in the range of (1400 to 400cm^{-1}) using a Jasco FT/IR-300E infrared spectrophotometer. The alkali halide disk-technique at room temperature was used. The polymers were mixed with well-dried infrared grade potassium bromide and then sufficiently ground to obtain a homogeneous mixture of minimum particle size. The mixture was mechanically pressed at 70-Mpa pressure in the form of disks.

3. Results and Discussion

3.1. Positron Annihilation Spectroscopy

The positron lifetime spectra for nonirradiated and gamma-irradiated CTA samples are analyzed in terms of three lifetime components to give the best variance ratio and most reasonable standard deviations. Each lifetime component is corresponding to the average annihilation rate of a positron in a different state. The shortest lifetime component (τ_1) belongs to the annihilation of p-Ps atoms, and the intermediate one (τ_2) arises from the free annihilation of positrons in the polymer matrix while the longest-lived component (τ_3) is attributed to the o-Ps atoms in free volumes of amorphous regions of polymer via the pick-off annihilation.

A semi-empirical approach based on a quantum mechanical model developed by Tao [31] for molecular liquids was used to correlate the o-Ps lifetime, τ_3, (in ns) to the radius, R, of a spherical cavity according to the relation [32]:

$$\tau_3 = 0.5\left(1 - \frac{R}{R_0} + \frac{1}{2\pi(2\pi R/R_0)}\right)^{-1} \quad (1)$$

where $R_0 = R + \Delta R$ and $\Delta R = 0.1656$ nm is the thickness of the homogenous electron layer in which the positron annihilates [25]. Thus the average of the o-Ps hole size $V_h = 4/3\pi R^3$, which is probed by the o-Ps lifetime (τ_3), can be calculated. The probability of the o-Ps formation is called intensity of the o-Ps (I_3) and it is proportional to the number of cavities in the investigated systems [33].

Gamma irradiation of CTA polymeric films shows a decrease in the free volume size. It leads to an obvious decrease in the ortho-positronium (o-Ps) lifetime with an increase in the intensity of o-Ps. Taking τ_3 as a measure of the free volume hole size and I_3 as a number of free volume holes, the lifetime of o-Ps and its intensity for the nonirradiated sample have been deduced to be τ_3 =1.827 ± 0.005 ns and I_3 = 10.68% ± 0.076%. The lifetime τ_3 associated with the pick-off process as a function of gamma irradiation doses is shown in Fig. 2.

It is known that bond lengths of C=O bonds are around 123 pm in carbonyl compounds while for C–O bonds are in the range of 143 pm. So if the irradiation does not alter the interstices positions between the carbonyl groups but only drives some C=O bonds to decompose and forming C–O bonds, accordingly the resultant spaces between different

carbonyl groups shrink. Beside the formation of free radicals, the shrinking of space interstices available in the polymer network minimizes the free volumes sizes. This situation would also lead to an increase in the rate of annihilation process which is associated with more detected intensity.

The obtained data of the lifetime (τ_3) and free volume size for gamma irradiation samples exhibits three regions as shown in Figs. (2a) and (2c). First, there is a smooth decrease to about 10kGy. The 8.7% decrease in τ_3 is related to the formation of free radicals and the 17.3% decrease in the free volume is due to of the formation of C-O bonds in the carbonyl group. The free volume sizes are estimated using Eq. (1) and is found to decrease from 80 to 67 Å^3 at 10 kGy. Second, an increase in I_3 is apparent up to 15 kGy. It remains constant with increasing the irradiation dose up to 25 kGy. As shown in Fig. (2b), I_3 shows an increase at the beginning up to 10 kGy. Such increase in I_3 is mainly attributed to the presence of carbonyl groups, which are created during irradiation [34]. With increasing the dose, a smooth decrease in I_3 is attained up to 15 kGy and is followed by leveling off up to 25 kGy, which is familiar for γ-irradiated polymers [35]. This behavior may indicate that the stability in the structure has been achieved.

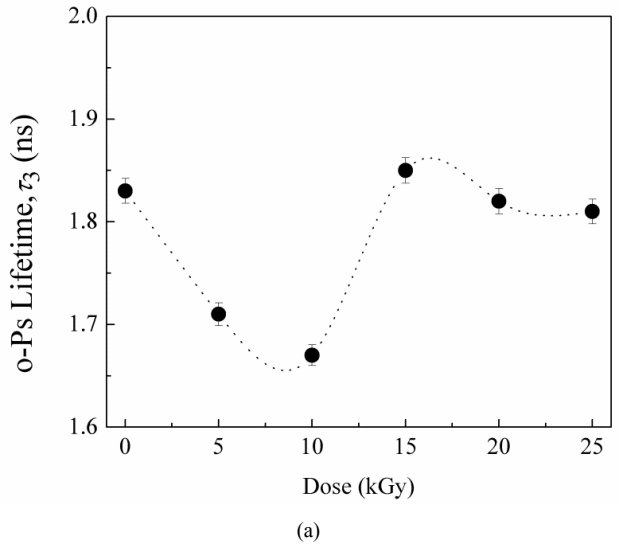
3.2. Thermogravimetric Measurements

In thermogravimetric method, TG curves, Fig. 3, are obtained at a heating rate of 10 C^o/min by using the expression:

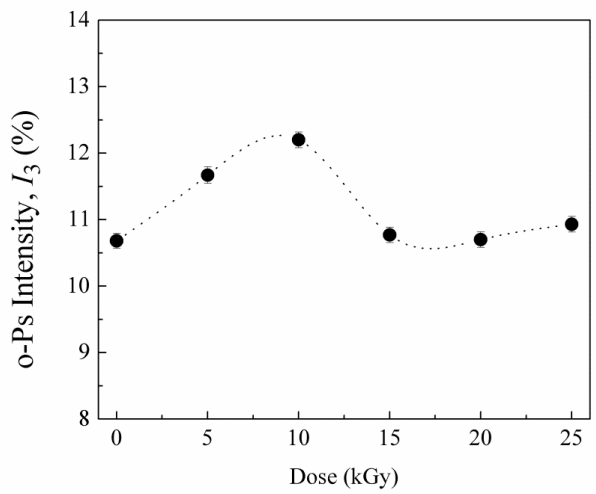
$$\ln\left[\ln\left(\frac{W_0-W_f}{W-W_f}\right)\right]=\frac{E_a\theta}{GT_s^2} \quad (2)$$

where G is the general gas constant, W_o and W_f are the initial and final weights of the stage, respectively. W is the remaining weight at a given temperature T and θ is the temperature difference between T and T_s, where T_s is the temperature which satisfies the equation:

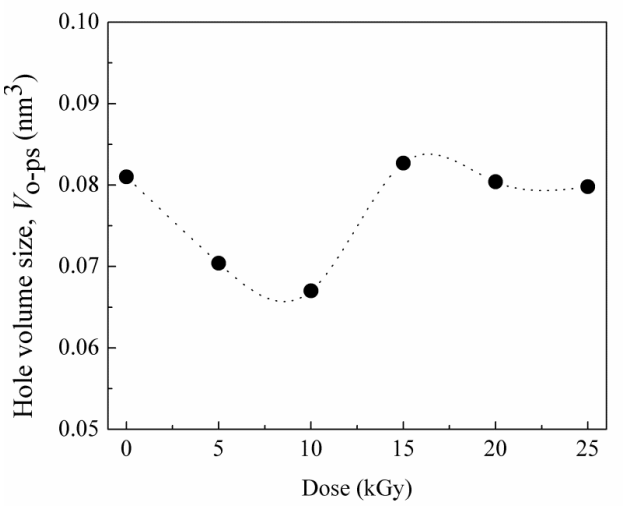
$$\frac{W-W_f}{W_0-W_f}=\frac{1}{e}=0.368 \quad (3)$$



(a)



(b)



(c)

Figure 2. Variation of lifetime, τ_3, (a), intensity, I_3, of the o-Ps component (b) and free volume size, V, (c) as a function of gamma doses

The plot of $\ln\left[\ln\left(\frac{W_0-W_f}{W-W_f}\right)\right]$ against θ leads to a straight-line relationship where the decomposed ratios are equal. Hence, the activation energy of decomposition E_a can be evaluated from the slope of the line.

Using the TGA thermograms, the values of onset temperature of decomposition T_o (the temperature at which the thermal decomposition starts) and activation energy of thermal decomposition (E_a) for CTA samples as a function of the gamma dose are calculated and are listed in Table 2. Fig. 4(a) shows the variation of (T_o) with the gamma dose. The figure shows that (T_o) decreases until a minimum value = 409.8℃ with a reduction reach to 0.78% at 10 kGy (sample 3). The figure indicates a decrease in thermal stability of the polymer samples due to degradation of carbonyl group associated with the development of C-O bonds and free radical formation. Then the thermal stability is increases as the gamma dose increases up to 20 kGy due to the formation of C=O bonds (cross linking process). The interpretation of these results may be that, at the dose 10 kGy

the free radicals are formed and can be used in chemical reactions that lead to cross-linking mechanism and formation of C=O bonds once again [36].

Using the TGA curves (Fig. 3), values of activation energy of thermal decomposition E_a are calculated for nonirradiated and irradiated CTA film samples (Table 1). Fig 4(b) shows the variation of E_a with the gamma dose. It is clear that E_a exhibits the same trend to that of T_o, and shows a decrease reaching a minimum value 3.32 eV with a reduction of 3.8% at 10 kGy which is attributed to chain session. After that, the variation of E_a is followed by an increase with the furtherer increasing of the gamma dose up to 20 kGy. Such increase in E_a values at these values of doses is maybe due to cross-linking mechanism [36].

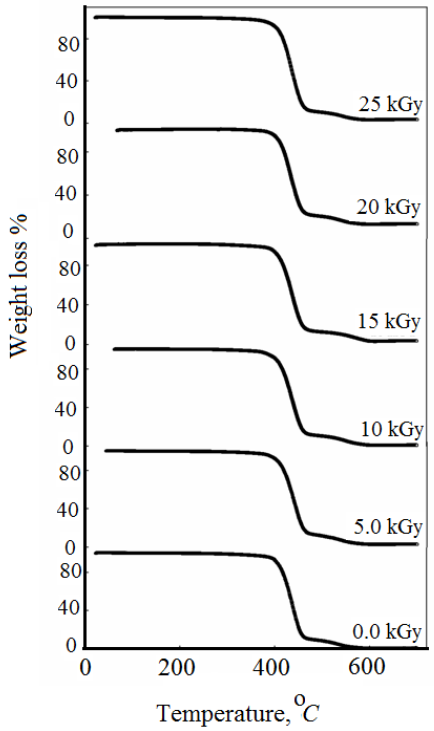
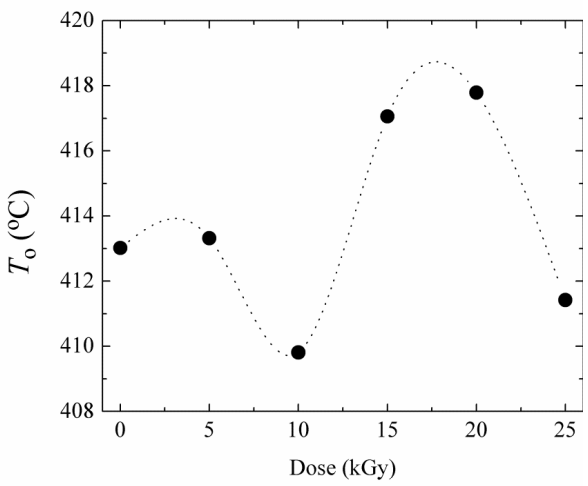
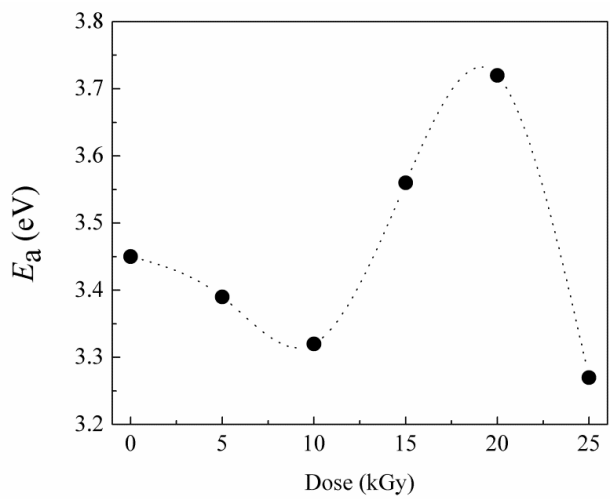


Figure 3. TGA thermograms measured in the temperature range of 20-700 °C for different investigated CTA samples



(a)



(b)

Figure 4. (a) Variation of onset temperature of decomposition, T_o, with the gamma dose, (b) Variation of activation energy of thermal decomposition, E_a with the gamma dose

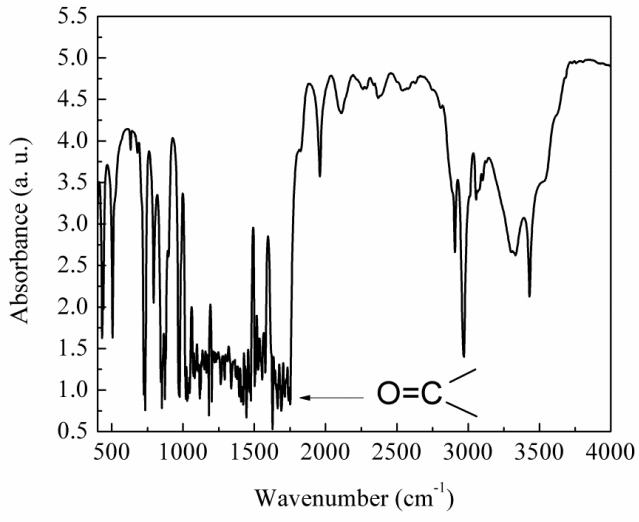


Figure 5. FT-IR spectrum of CTA sample

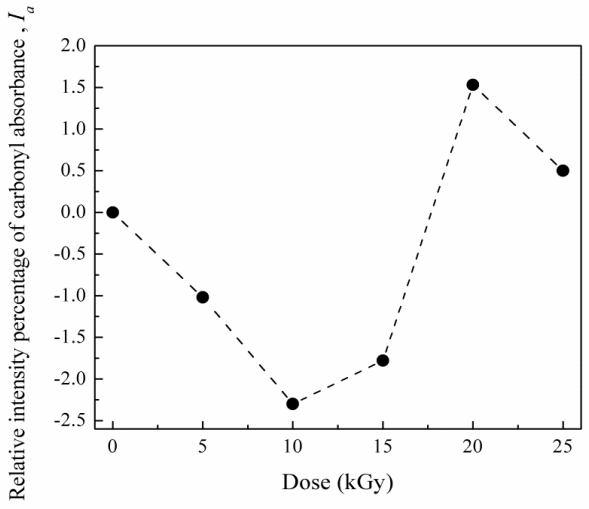


Figure 6. Variation in IR relative intensity percentage of CTA carbonyl absorbance as a function of the gamma irradiation doses

Table 1. Irradiation dose, positron lifetime, τ_3, intensity, I_3, and free volume size, V, onset temperature, T_o, and activation energy, E_a

S	Dose (kGy)	τ_3 (ns)	I_3 (%)	V (nm^3)	T_o (^oC)	E_a (eV)
1	0	1.83 (0.0121)	10.68 (0.112)	0.0810 (1.96×10^{-6})	413.02	3.45
2	5	1.71 (0.0111)	11.67 (0.125)	0.0704 (1.80×10^{-6})	413.32	3.39
3	10	1.67 (0.0101)	12.20 (0.117)	0.0670 (1.54×10^{-6})	409.81	3.32
4	15	1.85 (0.0125)	10.77 (0.116)	0.0827 (2.07×10^{-6})	417.06	3.56
5	20	1.82 (0.0123)	10.70 (0.117)	0.0804 (2.04×10^{-6})	417.79	3.72
6	25	1.81 (0.0120)	10.93 (0.119)	0.0798 (1.95×10^{-6})	411.42	3.27

3.3. FT-IR Measurements

Fig. 5 illustrates the measured absorbance for CTA spectrum in the IR region between 4000 – 400 cm^{-1}. Bands at 1219 and 1055 cm^{-1} are attributed to stretching modes of C-O single bond. CTA contains carbonyl group which absorbs in the region 1760-1665 cm^{-1} due to the stretching vibration of the C=O bond. This distinctive carbonyl band is particularly useful for diagnostic purposes because it has a characteristic high intensity. Fig. 6 shows the variation of intensity of IR carbonyl relative percentage of absorbance intensity (I_a) for irradiated and non-irradiated CTA samples as a function of the gamma irradiation doses. It is clear that I_a exhibits an oscillated changes in the relative percentage of absorption intensity of carbonyl bands. The observed changes in the relative carbonyl absorption bands are good sign of the effectiveness of the irradiation process even with these small irradiation doses. The carbonyl relative percentage of absorbance intensity, I_a, data exhibits three regions. First, there is a smooth decrease in I_a equal to 2.3% with increasing the dose up to 10 kGy. The decrease in the carbonyl relative percentage of IR absorbance intensity, I_a, means that the carbonyl group is partially dissociated. Subsequently as the dose increases, an increase of 1.5% in the carbonyl I_a is calculated up to a irradiation dose of 20 kGy. This increase is mainly due to the reformation of C=O bond of carbonyl groups relative to C-O bond numbers. Increasing of gamma irradiation more to 25 kGy leads to inflection point associated with a decrease in the I_a value.

The behaviors of preceding results are matching well with those of the positron annihilation spectroscopy and the thermogravimetric data, respectively. This means that the effect of radiation on CTA polymeric films could be explained in terms of the change in the internal network structure of CTA due to the change in the intermolecular interstitial space mainly between the carbonyl groups. Such intermolecular interstitial space change fluctuates effectively the sizes of available network free volumes as a result of dose-based transformation of C=O bonds into C-O bonds and vice verse. Thus irradiation dose-based reversible transformation may provide, at certain gamma doses, the possibility of formation of C-O bonds which associated free radicals sites. Creation of free radicals motivates an increase in the positron annihilation intensity with decreasing simultaneously the positron lifetime.

4. Conclusions

The sensitivity of positron annihilation spectroscopy detects successfully the variation on chemical microstructure of CTA polymeric films after low doses gamma irradiation. The different positron annihilation spectroscopic parameters (such as positron lifetime and intensity) depend on the state of the electron participating in the annihilation reaction and on the available free volumes as well. The results of thermogravimetric analysis and FT-IR spectroscopy confirmed the findings of positron annihilation spectroscopy. The explanation and analysis of the obtained data is afforded by the formation or decomposition of carbonyl group in CTA after gamma irradiation.

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