Study of Induced Chemiluminescence in Tracks Detector Exposed to Gamma Radiation During Thermal Treatments.

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Abstract

In this work, three independent chemiluminescence processes were found, through thermal degradation of gamma irradiated cellulose nitrate and cellulose acetate solid state nuclear tracks detectors. These processes can be summarized by:-

The low temperature induced chemiluminescence which depends on the absorbed dose, temperature and the composition of the surrounding atmosphere during irradiation. This weak chemiluminescence is attributed to the decay of charge transfer complex between oxygen and hydroxyl radicals formed in the detectors. Second process was a peak in chemiluminescence at 338^{o}K associated with decomposition of peroxide groups presents in the detectors .

Third process was, as temperature approaching 343^{o}K, an intense chemiluminescence was found to correlate with polymer chain scissions, resulting in the decrease in chain degree of polymer.

The above results show that chemiluminescence is a good tool to study radical degradation mechanisms. Also it explains why these detectors are not useful for gamma rays dosimetry.

Introduction

The degradation of polymer is far from being well understood and is still a subject of many recent studies in the field of polymer [1]. Two phases of this process may be distinguished: One below 573°K, which is of interest when the long-term stability of materials containing cellulose is examined. The degradation of cellulose that occurs in the presence of oxygen and in an inter atmosphere is essentially different; It is faster in oxygen. Additionally, cellulose additives influence the degradation both at elevated [2] and at nearly ambient conditions [3].

These effects of oxygen and temperature reflects that some chromophores exist in the polymer or a recombination polymer [4]. This study focused on the mechanism in which these charged centers created in the polymer annealed at temperatures below 573°K . The polymers under consideration are the well known nuclear tracks detectors cellulose nitrate (CN) and cellulose acetate (CA). Thermal degradation is on of the most terrible problems that facing dosimetry with detectors own polymeric structure [5]. The aim of this study is to obtain some knowledge about the relation between the chromosphores created in thermally treated solid state nuclear tracks detectors, irradiated with gamma radiation .By means of chemilminescence (CL). Induced by these chromophores.

Materials and Measurements.

Detector samples under study were from Whitman, Maidstone, UK. Chemiluminescence (CL) experiments were performed on photon counting instrument manufactured by Nuclear Enterprise, UK. CL reagents were supplied by Fluka, Switzerland. The measurements were carried out in different atmospheres by means of gas flow through the sample closed circuit glass cell. While thermal treatments were carried out onto a cupper pan in the sample compartment. And placed into Kottermann-3048 oven.

Irradiation experiments were done by Cs^{137} gamma source of activity 12 Ci as measured in the date of manufacering [6].

The degree of polymerization (DP) was determined according to the standard method [7]. Also peroxide groups were determined according to the method by Barnett [8].

Results and Discussion.

CN and CA detectors were irradiated to different dose of γ -rays at different temperatures. In order to study the CL yield originated by different doses, temperatures and atmospheric conditions, the CL signal were left to decay from some initial value tending to the background level, which is attained after approximately four hours. As the time of irradiation increase with any temperature, the initial CL intensities shift to the higher value. These intensities were proportional to the number of light-emitting particles.

Of particular interest is the temperature dependence of the integral light emitted from irradiated CN shown in (Fig. 1), and that for CN and CA shown in fig.(2).

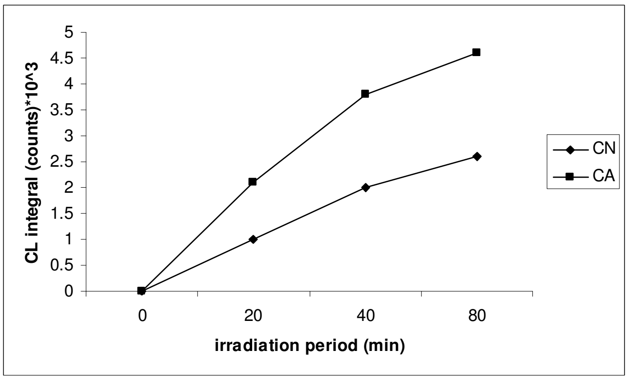

Fig.(2): CL integrals of irradiated CN and CA detectors at 303°K

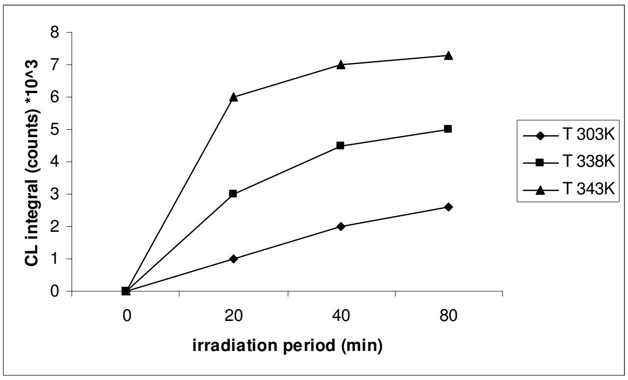

Fig.(1): Integral CL of irradiated CN detector at 303°K, 338°K, 343°K

The dependence is probably related to a higher mobility of particles induced by an increased temperature. From Fig. (1) and Fig. (2). an approximate formula can be estimated for CL intensity (I) at respective irradiation time (t) as:

$$I = I_s\ (1\text{-}e^{-kT}) \qquad \text{………………………} (1)$$

Were I_s is the saturation value for CL intensity. k: expressing how fast the ordinary CL level is attained with a given time of irradiation. I_s can be numerically fitted by math. Lab. programs, the equations:

$I_s = 17.6 – 500/RT$ for CA detector,

$I_s = 15.1 – 486/RT$ for CN detector.

Where T is the absolute temperature and R = 8.314 J/kmole. .

Equ. (1) Compose of both an exponential and a linear part. The exponential part varying faster than the linear one. This because of the effect of γ-rays generats reactive species on the surface, while the slower part due to that in the bulk. These radicals converting part of their energy to light [9]. This effect becomes pronounced in the presence of oxygen, which in order to get more information about the dependence of radicals that causing CL and irradiation, one must test CL intensity under different ambient conditions[10]. Easily adds to alkyl radicals and proxy radicals are formed. The recombination reaction of peroxyl radicals is considered as the main source of CL during oxidation of polymers [11]. Fig. (3) shows how the CL intensity depend on the pressure of O_2 in the surrounding atmosphere during irradiation ,where data pointed by (◊) the O_2 pressure is twice than in (□), and (Δ) irradiation processes were done in air, while (∗) irradiation was done in N_2 .

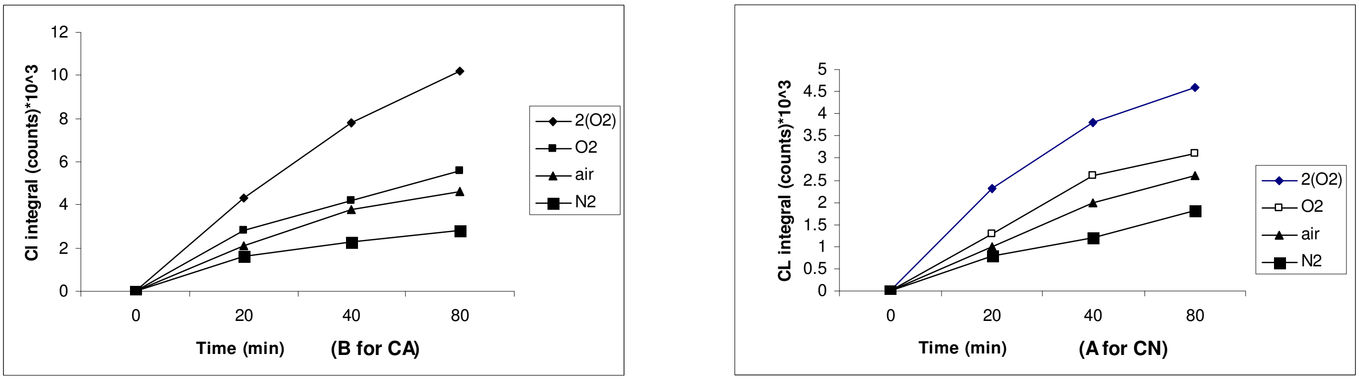

Fig.(3): A comparison of CL integrals Of CN and CA detectors after irradiation for the time periods indicated in O_2, air and N_2 at 303K

It is concluded form above data, that oxygen participates in the initial process of light emission interacting with some chromopher in the material [12]. A bimolecular termination of reacting particles is required at the same time. An idea of charge – transfer complex formed between atmospheric oxygen and peroxyl in the material induced by γ - rays, and subsequently destroyed by elevated temperature. The temperature induced decay of such charge transfer complexes should occur by way of irradiation.

When the same experiment is repeated for γ–ray dose 2Gy at 303°K in air with relative humidity 100%, the CL intensity decreases to 60% for CA and 68% for CN, with respect to the control samples (all samples were kept in darkness). The lower CL of the samples kept in humid atmosphere is an indication that absorbed water can either decompose the presumed charge transfer complexes or replace chemisorbed oxygen [13]. Since water has a plasticizing effect on CA and CN [14], so higher mobility of the species in the detector. This also led to a reduction in CL signal. The decay of CL signal is much slower in lab. atmosphere and temperature and also with longer half life. Fig. (4).

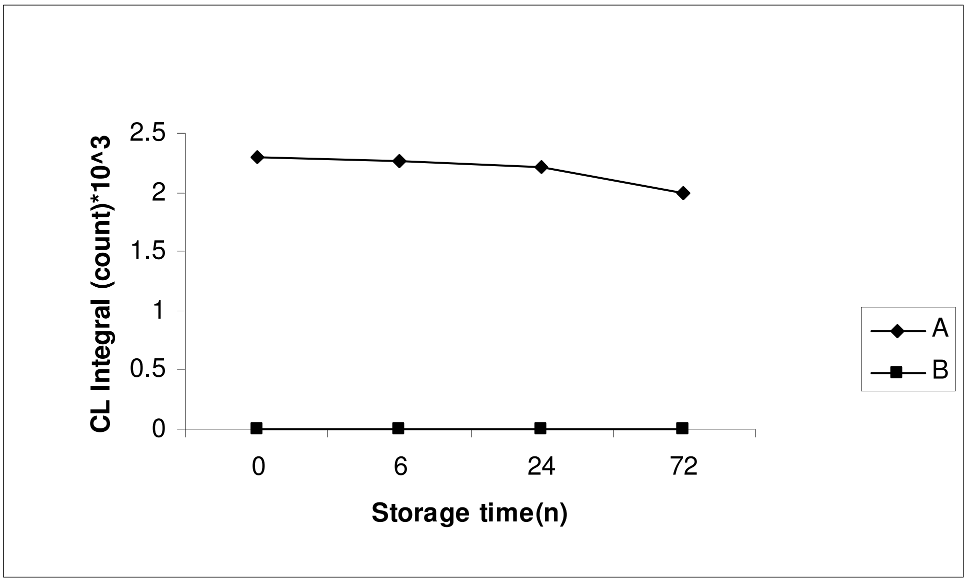

Fig.(4): CL integrals (CN) detectors (A) after irradiation (lh , air) and storge in air (in darkness) at ambient Temperature. The line (B) indicates the CL integral Of a non – irradated detector.

The second phenomena is due to various oxygen containing functional groups, can be introduced into a CN and CA molecules, which is due to temperatures between (338 – 343)°K and the same previous γ-rays doses, such as carboxyl and peroxide groups [15]. The thermal decomposition of peroxide groups as in Fig.(5), provides free radicals in the material, which mutual recombination lead to excited carbonyls converting part of their energy to light [16]

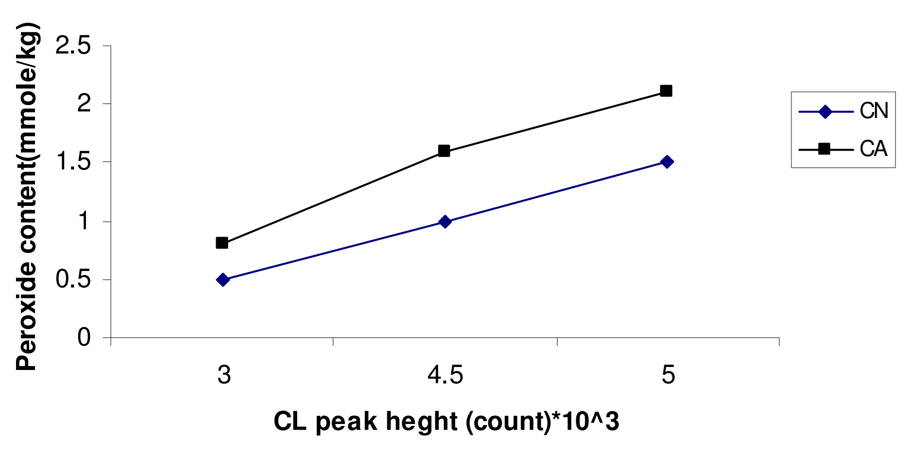

Fig.(5): Correlation of peroxide content determination with CL peak height at 338°K, for CN and CA.

As seen in Fig.(6), oxidized CN and CA ,it shows that every change of atmosphere from N_2 to O_2 is accompanied by rise in emission of light, while a slower decay in CL accompanies every switch to N_2 .

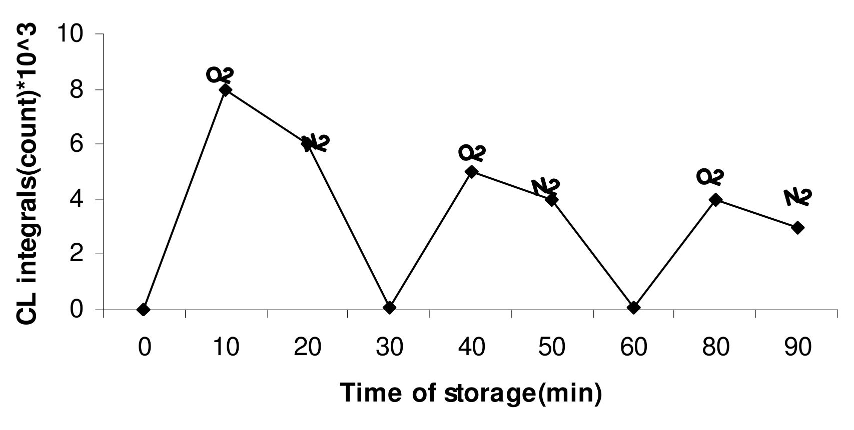

Fig.(6): Effects of changes of atmosphere between N_2 and O_2

On CL of a CN at 338^{o}K.

The relatively abrupt increase of CL after a switch from N_2 to O_2 is an indication that the process of accumulation and decomposition of peroxides, initiate free radicals sites involving a direct interaction of cellulous-oxygen, acetate – oxygen and nitrate – oxygen takes place. The process of sitting of some level of hydroperoxidos should have some distinct kinetics in the CL intensity time pattern. The switching from O_2 to N_2 shows these two types of initiation of cellulose (CA , CN) O_2 faster decay followed by the slower process corresponding to the gradual decomposition of peroxides. By comparing this process to that in hydrocarbon polymers [17]. Peroxides in CA, CN are more unstable, because they can decompose rapidly in a set of reactions induced by the neighboring hydroxyl groups [15]. The concentration of peroxides radicals were temperature dependent. A steady – state concentration of peroxides is achieved in 83 min, at 338^{o} K , which dose not indicate an increased reactivity when compared with hydrocarbon polymers [18] . Table (1). Shows a rapid steady –state formation even at 338^{o} K , whereas the low peroxide content indicates that the radical oxidation chain are short.

Table (1). Peak area under the glow curve vs. time oxidation at 338^{o}K.

Dry O_2 atmosphere		Air atmosphere (60% relative humidity)	
Time(min)	Peak area	Time(h)	Peak area
20	15	2	9.8
40	16.1	3.6	5.1
83	16.4	4.1	3.3

The process of oxygen atmosphere is actually composed of two superimposed process:

1-Observable also in nitrogen at higher temperature above 338°K.

2-Corresponds to the above mentioned process s of peroxide decomposition.

The role of moisture in the oxidation and its effect on the CL mechanisms was due to the plasticizer in the case of irradiated samples, where the CL intensity decreased due to the presence of water. Fig. (7), experiment done with moist detectors, shows not only a pronounced initial peak , but also a pronounced CL in O_2 as compared to the sample contain less absorbed water.

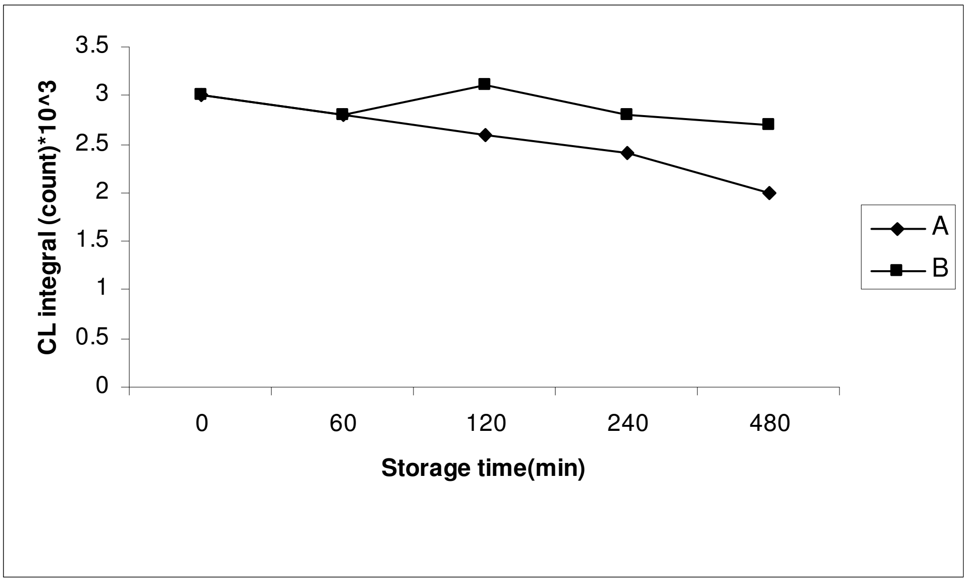

Fig.(7) : CL of CN detector at 338°K , irradiation in air .

A was kept in 100% relative humidity prior to Experiment, sample B at room.

The third CL phenomenon represents the elevated and steeply rising CL intensity as the temperature increase above 343°K. It occurs in N_2 as well as O_2 atmosphere. The intense CL at higher doses turns out to be a consequence of thermal instability of the components expressing the rate of sessions of bonds linking the glucopyranose unit in the molecule or the rate of session of bonds in primary degradation products if the transglycosylation reaction is the rate determining step. The changes in degree of polymerization during decomposition of CN and CA in N_2 at temperature between (348-358)°K have been followed by viscometry Fig. (8). The data were interpreted by assuming that the first – order random degradation of a linear polymer follows apparent zero-order kinetics as the initial stage of degradation process can be conveniently divided into three phases for which separate rates of chain session can be obtained – Apparent activation energies for the first and the second process for CN sample are 79 and 108 kJ/mole, while for CA samples are 71 and 99 kJ/mole respectively.

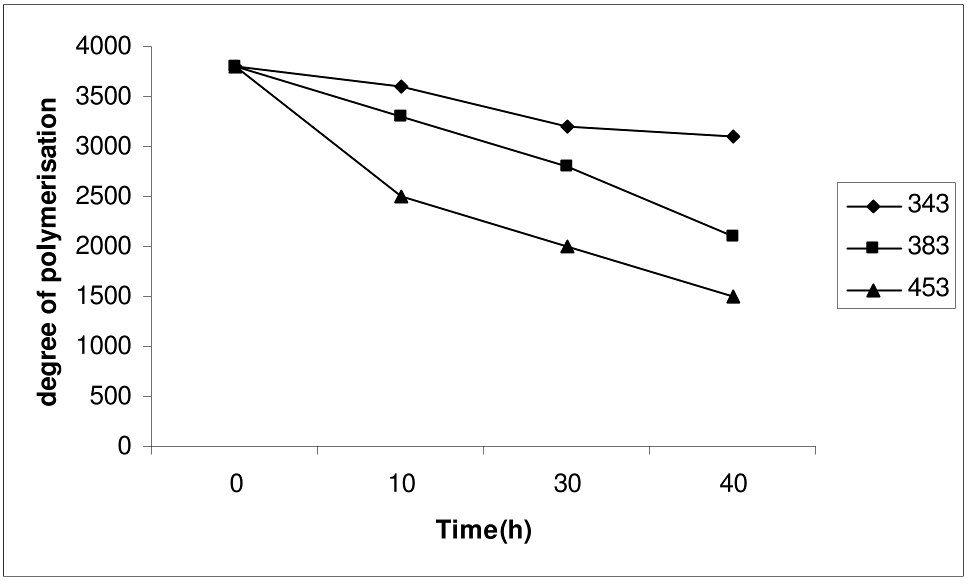

Fig. (8): Changes in degree of polymerization in CN samples in air at temperatures from 343°K to 453°k.

The comparison of these two setes of experiments namely of viscometric and chemiluminescence measurements performed under comparable condition, takes into account the fact that CL intensity time runs, are the rate curves expressing the rate of session of the weakest bonds in the main chain. Like C-O-C bonds alkyl and alcoxyl radicals can be formed, which can give excited carbonyl compound in mutual termination, partially converting their energy into emission of light [19]. The total conversion of bounds may found from the area under CL curve S_t. for each temperature. Then CL intensity I may be approximated by non-linear regression from fig.(8):

$$I = \frac{a_1}{(1+b_1t)^2} + \frac{a_2}{(1+b_2t)^2} \qquad ....3$$

Where I is CL intensity at any time t, and a1 , a2, b1 and b2 were found from curve fitting from fig.(8). The total area under CL curve after long time is:

$$S_\infty = \frac{a_1}{.b_1} + \frac{a_2}{b_2} \qquad \ldots\ldots\ldots\ldots 4$$

The resulting correlation between CL and viscometric data is shown in fig.(9) , and indicate that CL phenomenon can well be associated with chain scission and the correlation is not liner. From Fig. (9),the following empirical equation can be estimated by curve fitting:

$$1 - \frac{S_t}{S_\infty} = 1.0 - 4.1\ e^{-398Dp} \qquad \ldots\ldots\ldots\ldots 5$$

It is of interest that the zero coordinate is achieved at the abscissa value 0.26 and 0.22, which may express the limiting values of degradation of CN and CA detectors under the given conditions

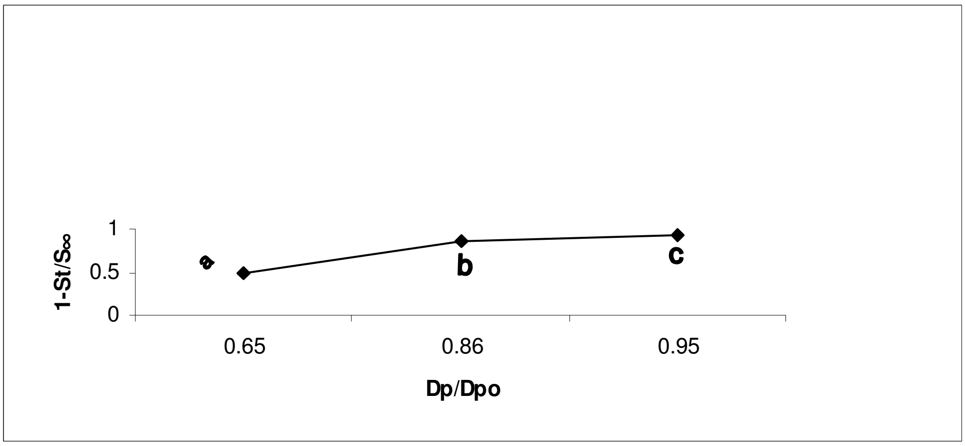

Fig.(9): Correlation of the area under CL curve and degree of polymainsation (Dp) data for CN at temperatures as indicated, S_t indicates integral CL signal for time t, S∞ indicates integrated CL signal for time Dpo is the initial degree of polymerization

Where a (T=453^{o}K) , b (T=363^{o}K) and c(T=348^{o}K)

Conclusion

CL measurements with CA and CN samples have revealed the following common features.

1-CL peaks during experiments in N_2 atmosphere can be attributed to the decomposition of presumed charge-transfer complex between O_2 and hydroxyl at peak with maximum at 303^o K and to the decomposition of peroxide groups presents in the sample. The peak with the maximum at 343^oK. Formation of the charge transfer complexes is induced by irradiation of the sample with γ-rays. While their decay taking place in the radiation path is induced by increasing temperature.

2-An intense CL during isothermal experiments at elevated temperatures may well be attributed to the chain-session reaction leading to free radicals intermediates

3-An overall more intense CL in atmosphere containing O_2 than in N_2 atmosphere, Which can be associated with the conversion of alkyl radicals to peroxyl radicals regardless of the more initiation.

4-Finally, an exponential correlation between the residual surface of CL intensity time runs and the degree of polymerization obtained for degradation experiments in N_2 for temperatures 348^oK to 380^oK is a confirmation of the potential of CL to given some new insight on the part of the mechanism of CN and CA degradation occurring by free radical mechanisms.

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دراسة التألق الكيميائي المحتث المعرض لاشعة كاما خلال المعالجات الحرارية

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الملخص

في هذا العمل شوهدت ثلاث عمليات تخص التألق الكيميائي المستقلة عن بعضها البعض , خلال التحلل الحراري للعينان المكونة من نترات السليلوز واسيتان السيليلوز المعرضة لاشعة كاما . وهذة المواد معروفة جيدا" للمشتغلين في مجال التقنين الاشعاعي بواسطة كواشف الاثر النووية الصلبة . والعمليات الثلاثة تلخص بما يأتي : التألق الكيميائي المحتث في درجات الحرارة الواطئة والذي يعتمد على قيمة الجرعة الممتصة , درجة الحرارة , مكونات الجو المحيط للعينة خلال عملية التشعيع . ان هذا التألق ناتج انفصال الشحنات بين جذور الاوكسجين والهيدروكسيل المتكونة في الكاشف . اما عملية التألق الثانية تمثل قمة التألق المتكونة عند درجة حرارة ٣٣٨كلفن والتي تتكون بسبب تفكك مجموعة البروكسيد الموجودة في الكاشف .

اما العملية الثالثة فأن شدة التألق ستزداد كثيرا" عند درجة حرارة ٣٤٣ كلفن وذلك بسبب بداية تفكك السلاسل البوليرية .ويسبب في نقصان درجة البلمرة .

ان النتائج اعلاه توضح ان التألق الكيميائي يعتبر اداة جيدة لفهم ودراسة ميكانيكية الاغلال الكيميائية للمواد . وبنفس الوقت يعطي تفسيرا" واضحا" لماذا لاتستعمل مثل هذه الكواشف للتقنين الاشعاعي لاشعة كاما.