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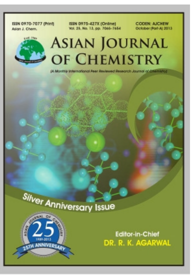

Influence of γ-Ray Irradiation on the Thermal Stability and Conductivity of Polyfuran

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The γ-radiation effects on the conductivity and thermal properties of polyfuran were investigated. The polymerization reaction of furan was carried out at 40 ºC in the presence of $FeCl_3$. Then the polymer obtained was irradiated by γ-radiation at absorbed doses of 1, 5 and 10 kGy. The unirradiated and irradiated polyfuran samples were investigated comparatively for conductivity, structural and thermal properties by means of four point probe measuring system, Fourier transform infrared and thermogravimetry, respectively. The conductivities of the polymer irradiated with γ-radiation seem to be smaller than that of unirradiated polyfuran. The conductivity values of the irradiated polyfuran films decreased with the rising absorbed doses of γ-radiation. The TG curves showed that both unirradiated and irradiated polyfuran decomposed thermally in three stages and remained *ca.* 55 (unirradiated), 49 (1 kGy), 46 (5 kGy) and 40 (10 kGy) percent undecomposed at 600 ºC. The apparent activation energies were calculated by the following differential (Kissinger) and integral (Flynn-Wall-Ozawa (FWO)) methods. The activation energies of the main decomposition stage for unirradiated and 10 kGy irradiated polyfuran were found by the Kissinger method to be 351.1 and 268.9 kJ/mol, while by Flynn-Wall-Ozawa they were 360.9 and 271.0 kJ/mol, respectively.

Key Words: Polyfuran, Gamma radiation, Conductivity, Thermal degradation.

INTRODUCTION

Polymers based on heteroaromatic monomers such as polythiophene, polypyrrole, polyaniline and polyfuran have received considerable attention due to their interesting electrical, electrochemical, structural, mechanical and optical properties[1,2]. They have many applications as light-emitting diodes[3,4], batteries[5], corrosion protection[6], ion sieving[7] and sensors[8-10] in scientific and technological areas.

Less study on polyfuran [P(Fu)] has been reported in the literature, compared to that of polypyrrole and of polythiophene. Polyfuran conducting polymers can be synthesized by both chemical and electrochemical methods in organic media. Various copolymers and composites of polyfuran such as polyfuran with Al_2O_3 and montmorillonite clay[11], polyfuran with acetylene black[12], polyfuran/poly(2-fluoroaniline)[13], furan and 3-methyl thiophene[14] *etc.* have been prepared to develop the properties of individual polymers.

In addition, polyfuran can be used as a humidity sensor and optoelectronic device since its electrical resistivity decreases considerably and reversibly upon contact with moisture and upon doping the colour changes from yellow-brown to black-brown, respectively[15,16].

The study of conductivity and thermal behaviour of various polymers irradiated with different forms of radiation, *e.g.* protons, neutrons, electrons and γ-rays is of great interest[17-19]. Thermal studies on polymeric materials have great importance since the different thermal properties of a polymer are strongly dependent on its internal structure. Irradiating a polymer destroys its initial structure by way of crosslinking, free radical formation, irreversible bond cleavages *etc.*, resulting to the fragmentation of the polymer molecule and formation of saturated and unsaturated groups. The effects of radiation on thermal properties of some polymers have been reported by several research groups. Sinha *et al.*[20] have studied the radiation-induced modification of thermal properties of Homalite, American-acrylics, Lexan, Makrofol-E, polycarbonate, triafol-TN, triafol-BN and polypropylene. The thermal and electrical behaviours of radiation vulcanized EPDM/Al_2O_3 composites have been reported by Abdel-Aziz *et al.*[21].

It is important to study the degradation of the polymers in understanding their usability for processing, application and thermal recycling. The influence of γ-radiation on the thermal stability of polyfuran has not yet been studied. Therefore, the present work aimed to study the changes in the conductivity and thermal properties of irradiated polyfuran in comparison to that unirradiated.

Kinetic methods[22-24]: Thermogravimetric analysis is used to study the degradation kinetics of the polymers. In general, the thermal degradation reaction of a solid polymer is represented as follows

$$A_{solid} \rightarrow B_{solid} + C_{gas}$$

where A_{solid} is the initial material, B_{solid} and C_{gas} are the solid residue and the gas product, respectively.

The following basic rate equation is used for the thermal degradation of polymers under an inert gas atmosphere such as nitrogen

$$r = \frac{d\alpha}{dt} = k(T)\times f(\alpha) \tag{1}$$

where T is the absolute temperature (K), r is the change in the degree of conversion (α) per unit time (t) or the rate of degradation and f(α) is the conversion function (the reaction model). The degree of conversion (α) is calculated by eqn. 2, where m, m_o and m_f are the actual, initial and final masses of the sample, respectively.

$$\alpha = \frac{(m_o - m_t)}{(m_o - m_f)} \tag{2}$$

k is the reaction constant which can be expressed by the Arrhenius equation:

$$k(T) = Ae^{-(E/RT)} \tag{3}$$

where A, E, R and T represent pre-exponential factor, activation energy, gas constant and temperature, respectively.

By combining eqns. 1 and 3 the following equation is obtained

$$\frac{d\alpha}{dt} = Ae^{-(E/RT)} \times f(\alpha) \tag{4}$$

According to non-isothermal kinetic theory, the degree of conversion α is expressed as a function of temperature which is dependent on the time of heating. Thus the heating rate (β) can be described as

$$\beta = \frac{dT}{dt} \tag{5}$$

Eqn. 4 is modified as follows

$$\frac{d\alpha}{dt} = \left(\frac{1}{\beta}\right) Ae^{-(E/RT)} \times f(\alpha) \tag{6}$$

The eqns. 4 and 6 form the basis of many equations derived to evaluate thermal analysis data.

Several integral and differential methods are used for the calculation of the kinetic parameters A, E and n. Kissinger (differential) and Flynn-Wall-Ozawa (integral) methods were used in this work.

Kissinger method[25]: The activation energy is calculated by this method ignoring the reaction mechanism through the following equation (eqn. 7)

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \ln\left(\frac{AR}{E}\right) + \ln(n(1-\alpha_{max})^{n-1}) - \left(\frac{E}{RT_{max}}\right) \tag{7}$$

where β is the heating rate, T_{max} is the temperature related to maximum reaction rate, A is pre-exponential factor, α_{max} is the maximum degree of conversion, n is the reaction order. Plotting ln (β/T^2_{max}) *versus* ($1000/T_{max}$) gives E activation energy from the slope.

Flynn-Wall-Ozawa (FWO) method[26,27]: This is one of the integral methods which enables determining the activation energy without considering the reaction mechanism. Pre-exponential factor (A) and activation energy (E) do not depend on the degree of conversion while they do on the temperature. This method uses eqn. 8.

$$\log g(\alpha) = \log\left(\frac{AE}{R}\right) - \log\beta + \log p\left(\frac{E}{RT}\right) \tag{8}$$

Doyle approximation is used and eqn. 9 can be obtained

$$\log\beta = \log\left(\frac{AE}{R}\right) - \log g(\alpha) - 2.315 - 0.4567\left(\frac{E}{RT}\right) \tag{9}$$

where the plot of log β *versus* 1000/T should give a straight line with the slope E/R whence E is obtained.

EXPERIMENTAL

The polymerization of furan (12 mmol) was initiated by the dropwise addition of the oxidizing agent ($FeCl_3$, 30 mmol) in chloroform under constant stirring at 40 ºC. The solid polymers were obtained by precipitating with methanol. The precipitates of polymer were separated and dried in vacuum oven at 50 ºC. Polyfuran pellets were prepared *ca.* 0.5-1.0 mm in thickness. The irradiations of the polymer pellets were carried out at room temperature. The polyfuran samples were irradiated at the different absorbed doses of 1, 5 and 10 kGy with γ-ray. FTIR spectra of the polyfuran were taken on Perkin Elmer spectrum 100 FT-IR spectrometer using KBr pellets. The conductivity measurements were obtained by means of Four Point Probe Measuring System. The TG curves were recorded by using a Perkin Elmer, Diamond TG/DTA. The samples were heated under N_2 atmosphere over a temperature range 30-600 ºC with a heating rate of 10 ºC min^{-1}. The weight loss (TG curve) and its first derivative (DTG curve) *vs.* temperature were recorded simultaneously.

RESULTS AND DISCUSSION

The γ-radiation effects on the conductivity and thermal properties of polyfuran have been investigated. The polymerization reaction of furan has been carried out in presence of $FeCl_3$ at 40 ºC.

The FTIR spectra of unirradiated and irradiated polyfuran at different absorbed doses such as 1, 5, 10 kGy are shown in Fig. 1a-d, respectively. The bands located between 3000 and 2850 cm^{-1} refer to the existence of aliphatic C-H bonds, while the bands located at 1700 and 1600 cm^{-1} indicate the existence of C=O bonds and isolated C=C bonds, respectively. Some ring openings are considered to occur due to the existence of C=O bonds in the IR spectra of polyfuran. The bands shown in the IR of polyfuran between 1100 and 1000 cm^{-1} are attributed to C-H bending and stretching. Those near 790 and 650 cm^{-1} are probably due to aromatic C-H out of plane bending.

The conductivity values of the polyfuran both unirradiated and irradiated at different absorbed doses are given in Table-1, the conductivities of unirradiated and irradiated (1, 5, 10 kGy) polyfuran were found to be 35.10^{-4} and 12.10^{-4} S cm^{-1}, respectively which indicates that the conductivity decreases with the increasing doses of irradiation (Table-1). The apparent decrease

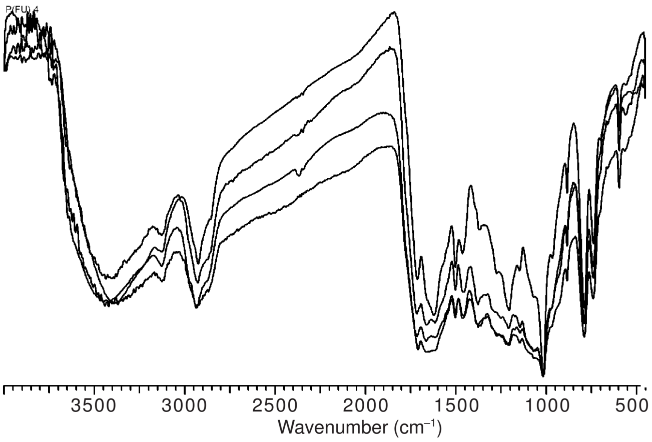

Fig. 1. FTIR spectra of the unirradiated and irradiated polyfuran at different absorbed doses. (a) unirradiated and irradiated by (b) 1 kGy (c) 5 kGy (d) 10 kGy doses

TABLE-1
CONDUCTIVITY VALUES FOR UNIRRADIATED AND IRRADIATED POLYFURAN AT DIFFERENT ABSORBED DOSES

Material	Conductivity (S cm^{-1})
Unirradiated P(Fu)	35×10^{-4}
Irradiated 1 kGy P(Fu)	31×10^{-4}
Irradiated 5 kGy P(Fu)	25×10^{-4}
Irradiated 10 kGy P(Fu)	12×10^{-4}

in conductivity may be attributed both to a decrease in the stability of the polymer and a lack of backbone conjugation.

The conductivity values of polyfuran synthesized by both electrochemical and chemical methods take place in the intervals of 80 to10^{-6} and 10^{-3}-10^{-9} S cm^{-1}, respectively as listed by González-Tejera *et al.*[2]. The differences in conductivity values of polyfuran occur due to the different reaction conditions such as temperature, solvent system, type of electrode, catalyst, *etc*. The conductivity value of unirradiated polyfuran in the present study is in good agreement with that given in previous workers[28].

The TG and DTG thermograms of polyfuran unirradiated and irradiated at different absorbed doses taken under N_2 atmosphere over a temperature range 30-600 ºC with the heating rates of 10 ºC min^{-1} are shown in Fig. 2a-d. The TG curves showed that the thermal decomposition of polyfuran samples at different absorbed doses occurred in three stages and approximately 55 (unirradiated), 49 (1 kGy), 46 (5 kGy) and 40 (10 kGy) per cent of the polymer remained undecomposed at 600 ºC. The analysis of thermodestruction of polyfuran was described by Gok *et al.*[29]. They reported the thermal degradation in three steps. The first step is assumed to be the loss of small units such as solvent and monomer in the polymers. The second step indicates the removal of the dopant anions from the polymer structure. The final step shows degradation of the polymer.

By comparing the thermal stabilities of both unirradiated and irradiated polyfurans it is shown that the thermal stability decreased by irradiation.

Thermal degradation kinetics of the polymers: Evaluation of the activation energy of thermal decomposition is useful for studying the thermal stability of the materials. To calculate the activation energy of 10 kGy irradiated and unirradiated polyfuran, the TG measurement of the polymers were performed under various heating rates such as 5, 10, 15 and 20 ºC min^{-1} in a temperature range of 30-600 ºC. Various thermogravimetric methods based on either the degree of conversion or the heating rate have been reported to determine the thermal kinetic parameters. The method proposed by Kissinger[25] and Flynn-Wall-Ozawa[26,27] have been used in the present study to calculate the activation energies.

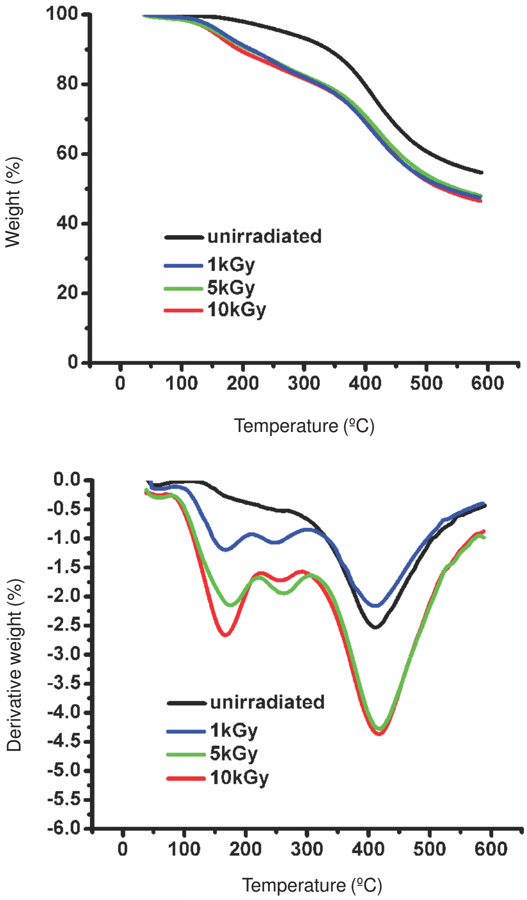

Fig. 2. TG and DTG of the unirradiated and irradiated polyfuran at different absorbed doses (a) unirradiated (b) 1 kGy (c) 5 kGy (d) 10 kGy

As mentioned above, Kissinger's method involves the temperature at the maximum rate of weight loss, T_{max}, obtainable from the DTG curve. The calculated activation energies with correlations obtained from the Kissinger method for unirradiated polyfuran are 159.6 kJ/mol (r^2 = 0.946), 199.8 kJ/mol (r^2 = 0.919) and 351.1 kJ/mol (r^2 = 0.967) while those for 10 kGy irradiated are 127.1 kJ/mol (r^2 = 0.992), 159.9 kJ/mol (r^2 = 0.989) and 268.9 kJ/mol (r^2 = 0.993) for the first, second and third stages, respectively.

The plots of ln β *versus* 1000/T of the Flynn-Wall-Ozawa methods are given in Fig. 3a for the unirradiated and 3b for 10 kGy irradiated polyfuran. The calculated results for the Flynn-Wall-Ozawa method in the 45-5 % conversion range are listed in Table-2. The mean activation energies calculated by Flynn-Wall-Ozawa method for the unirradiated polyfuran were found to be 179.6, 259.7 and, 360.9 kJ/mol while those for 10 kGy irradiated one to be 137.8, 167.5 and 271.0 kJ/mol for the first, second and third stages, respectively. The activation energies obtained by Kissinger method are lower than those

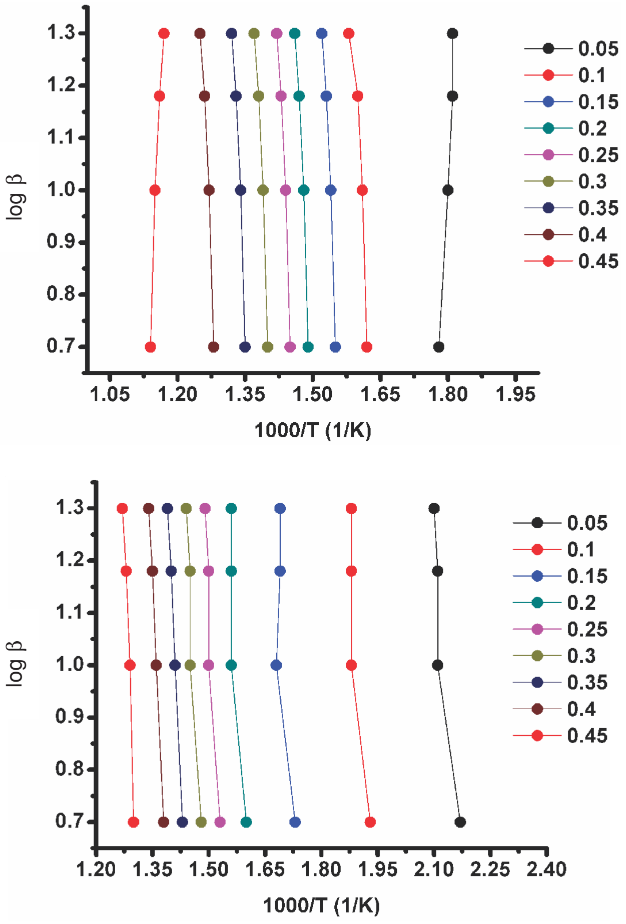

Fig. 3. Typical plots of log β *vs.* 1000/T (K) at several degree of conversion values in the range 0.05-0.45 % in 5 % intervals (a) unirradiated (b) 10 kGy

TABLE-2
DEGRADATION ACTIVATION ENERGIES OF IRRADIATED WITH 10 kGy AND UNIRRADIATED POLYFURAN CALCULATED BY FWO METHOD

	α	Unirradiated P(Fu)		Irradiated P(Fu) with 10 kGy	
		E(kJ)/mol	r^2	E(kJ)/mol	r^2
First stage	0.05	179.6	0.961	137.8	0.861
	Mean	179.6	–	137.8	–
Second stage	0.10	259.7	0.989	167.5	0.961
	Mean	259.7	–	167.5	–
Third stage	0.15	360.9	0.961	164.9	0.906
	0.20	360.9	0.994	209.4	0.997
	0.25	360.9	0.988	261.4	0.960
	0.30	360.9	0.961	261.4	0.960
	0.35	360.9	0.961	278.0	0.982
	0.40	360.9	0.961	360.9	0.915
	0.45	360.9	0.925	360.9	0.997
	Mean	360.9	–	271.0	–

by Flynn-Wall-Ozawa method. This is probably because the second peaks on DTG curves used in Kissinger method are not sharp enough to determine the peak point $T_{max.}$

Both Kissinger and Flynn-Wall-Ozawa methods indicate that the activation energy of unirradiated polyfuran is higher than those of irradiated ones as readily seen in the thermograms. This confirms that irradiation causes to cease the polymer bonds.

Conclusion

The possible effects of γ-radiation on the conductivity and thermal properties of polyfuran have been investigated. The conductivities of all the polymer samples irradiated by γ-radiation seem to be lower than that of unirradiated one. The conductivities of the irradiated polymer decreased with rising γ-radiation absorbed doses. The TG curves showed that the thermal degradation of polyfuran occurred in three stages the activation energies of which were determined comparatively from the experimental thermogravimetric data by both Kissinger and Flynn-Wall-Ozawa methods. The main step activation energies obtained by Kissinger method for unirradiated and 10 kGy irradiated polyfuran are 351.1 and 268.9 kJ/mol, while those calculated by Flynn-Wall-Ozawa method were found to be 360.9 and 271.0 kJ/mol, respectively.

Both Kissinger and Flynn-Wall-Ozawa methods indicate that the activation energy of unirradiated polyfuran is higher than those of irradiated ones which verifies the fact polymer bonds to be ceased by irradiation.

Consequently, conductivity and thermal analysis results show that the influence of γ radiation on the polyfuran may lead to cease in polymer bonds resulting a lower degree of backbone conjugation.

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