

Effects of a Hindered Amine Stabilizer (HAS) on Radiolytic and Thermal Stability of Poly(methyl methacrylate)

Katia Aparecida S. Aquino, Elmo S. Araujo

Departamento de Energia Nuclear, Universidade Federal de Pernambuco, Av. Prof. Luiz Freire, 1000, 50740-540, Recife/PE, Brazil

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ABSTRACT: Commercial Poly(methyl methacrylate) (PMMA) containing Tinuvin 622, a Hindered Amine Stabilizer (HAS), in 0.3% (wt/wt) concentration was investigated. The samples were irradiated with gamma radiation (^{60}Co) at room temperature in air. The viscosity-average molecular weight (M_v) was analyzed by viscosity technique. Both control PMMA (without HAS) and PMMA + 622 (with HAS) showed a decrease in molecular weight with the increase in dose, reflecting the random scissions that occurred in the main chain. The G value (scissions/100 eV of energy transferred to the system) was also obtained by viscosity analysis. G value results showed that the addition of Tinuvin 622 into the PMMA matrix significantly decreased the number of scissions/100 eV at dose range of 0–60 kGy. Analysis of infrared spectra showed a decrease in the carbonyl index (CI) in irradiated samples.

However the CI decrease was found lower for PMMA + 622 than for control PMMA sample. Thermogravimetric analysis (TGA) revealed that maximum decomposition temperature of additive PMMA is 42°C higher than control PMMA for unirradiated system. On the other hand this difference is not significant in irradiated systems at 60-kGy irradiation dose. The activation energy of the thermal degradation of PMMA was 165 kJ/mol, this activation energy increased 60 kJ/mol when Tinuvin 622 was added to PMMA matrix. Therefore Tinuvin 622 is a suitable radio-stabilizing agent for commercial PMMA in a 0–60 kGy dose interval. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 401–407, 2008

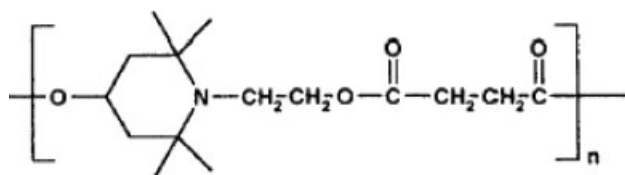
Key words: PMMA; additive; gamma irradiation; thermal degradation; activation energy

INTRODUCTION

Commercial poly(methyl methacrylate), PMMA, is used in the manufacture of medical supplies. Gamma irradiation at 25-kGy dose is the standard method for sterilization of plastic medical artifacts.¹ During PMMA irradiation, both electronic excitation and ionization produce excited atoms and ions which lead to the release of side groups such as H^\bullet , CH_3^\bullet , $\text{CH}_3\text{OOC}^\bullet$ and main chain scission.² Thus stabilization of PMMA matrix is necessary, to prevent major molecular damage caused by gamma irradiation process.³

Hindered amine stabilizers (HAS) are additives used in many resins as radical scavengers and antioxidants to protect the material against UV degradation. It is generally accepted that the decomposition of polymers initiated by ionizing radiation proceeds comparably to UV-induced degradation, i.e., via free radical mechanism.⁴ The efficiency of HAS additives

depends on their molecular weight, structure, solubility and concentration in the polymer matrix.⁵ Conversion of amines into nitroxyl radicals following the reaction with peroxy radicals leads to relatively stable intermediate species.⁶ Regeneration of the nitroxyl radical limits the consumption of HAS during degradation⁴ allowing the use of these additives in low concentration. Tinuvin 622 is a macromolecular HAS which exhibits a quite high thermal stability. This additive starts to decompose around 400°C with intramolecular ester group rearrangement. Final decomposition events occur at 900°C and include nitrile and hydrogen cyanide formation.⁷ The chemical structure of Tinuvin 622 is:



Correspondence to: K. A. S. Aquino (aquino@ufpe.br).
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The thermal degradation of PMMA, has been studied extensively.^{8–11} Radicals might play an important role in the degradation process of PMMA. They can be generated in PMMA by both thermal

degradation and decomposition initiated by ionizing irradiation process.

In the present work, the action of Tinuvin 622 as a stabilizing agent against radiolytic and thermal degradation of commercial PMMA was investigated. From determination of molecular weight, by means of viscosity technique, the G values (number of events/100 eV at absorbed energy) of PMMA and PMMA+HAS were obtained, whereas the effects of Tinuvin 622 on thermal degradation of PMMA was studied by thermogravimetric analysis.

EXPERIMENTAL SECTION

Materials

Amorphous commercial PMMA (Resarbrás Acrílicos, Brazil, $M_w = 95,000$ g/mol, 0.1 wt % of a processing additive) was supplied in the test specimens form (81 mm \times 140 mm \times 3 mm). According to manufacturer, the commercial PMMA was obtained by free radical polymerization (suspension). A distinct set of commercial PMMA test specimens containing 0.3% (wt/wt) of Tinuvin 622 (Ciba Especialidades Químicas Ltda, Brazil) was also supplied (PMMA + 622). This concentration is reported to stabilize PMMA films exposed to gamma irradiation.³

The specimens were irradiated at room temperature (about 27°C) in air, on a Gammacell Co-60 source at dose rate of 7.5 kGy/h, in doses varying from 10 to 60 kGy.

Viscosimetric analysis

The viscosity measurements of PMMA were carried out in methyl-ethyl-ketone (MEK) solution at 25.0°C \pm 0.1°C using an Ostwald viscometer in a thermostatic bath. The viscosity of the samples was calculated from the relative viscosity, $\eta_{rel} = v/v_0 \cong t/t_0$, where v and v_0 are the cinematic viscosities on the polymer solution and the solvent, respectively. The t and t_0 are flow times of solution and solvent, respectively. Therefore, η_{rel} was calculated from t/t_0 ratio. The specific viscosity ($\eta_{sp} = \eta_{rel} - 1$) and the reduced viscosity ($\eta_{red} = \eta_{rel}/c$), where c is the concentration of the solution, were calculated as well. The intrinsic viscosity $[\eta]$ was determined by the usual method of extrapolation using the reduced viscosity extrapolation curve plotted as a function of the concentration.^{12,13} The viscosity average molecular weight, M_v , was calculated from the corresponding $[\eta]$ values through the Mark-Houwink equation:¹⁴

$$[\eta] = K M_v^a \quad (1)$$

where K and a are 6.8×10^{-5} dL/g and 0.72, respectively, for the MEK-PMMA system at 25°C.¹⁵

The ionizing radiation effect on the polymer is expressed as a function of the G value. The relationship between M_v , G , and dose (in kGy) was obtained by Araujo et al.¹⁶ For PMMA the expression is:

$$10^6/M_v = 10^6/M_{v0} + 0.0566 G.D \quad (2)$$

where M_v and M_{v0} are the viscosity average molecular weight before and after irradiation, respectively, and D is the dose. The relationship is linear and provides the G value from the slope of the curve obtained by $10^6/M_v$ versus D . The linear interval guarantees that events are random and only under this condition eq. (2) can be used. Radiostabilizing action of Tinuvin 622 on PMMA matrix can be assessed by comparison of degradation index (DI) parameter ($DI = M_{v0}/M_v - 1$) for a determined irradiation dose. The DI is obtained from viscosity analysis and reflects the number of main chain scission per original molecule after irradiation. From this value is possible to calculate the protective factor (P) [eq. (3)] which indicates the reduction in yield of chain scissions in PMMA macromolecules containing Tinuvin 622 into polymer

$$P = G_c - G_a/G_c \quad (3)$$

G_c and G_a are the G value calculated for control PMMA and PMMA + 622, respectively.

Spectroscopic analysis

FTIR spectroscopy measurements were carried out on KBr pellets in the range 4000–400 cm^{-1} (Bruker IF 566 FTIR Spectrophotometer) in absorbance mode. ^1H NMR spectra of PMMA were obtained with a Varian Unity Plus, 300 MHz with CDCl_3 as solvent.

Thermogravimetric analysis

The weight loss of the samples was measured by using a TGA-50 SCHIMADZU thermoanalyzer, heating rate 10°C/min in nitrogen atmosphere (10 mL/min). DTG results were obtained by taking the time derivate, $d(W/W_0)/dt$, of the ratio of the sample weight, W , to the initial weight, W_0 .

TGA was also used to calculate the activation energy of the thermal decomposition reaction of PMMA, E_a . Thermal degradation of homogeneous system has the following expression at a specific heating rate, β :¹⁷

$$d\alpha/dt = (A/\beta)\exp(-E_a/RT)(1 - \alpha)^n \quad (4)$$

where A is the Arrhenius pre-exponential factor, E_a is the activation energy of degradation process, R is the ideal gas constant, and T is the temperature. Fur-

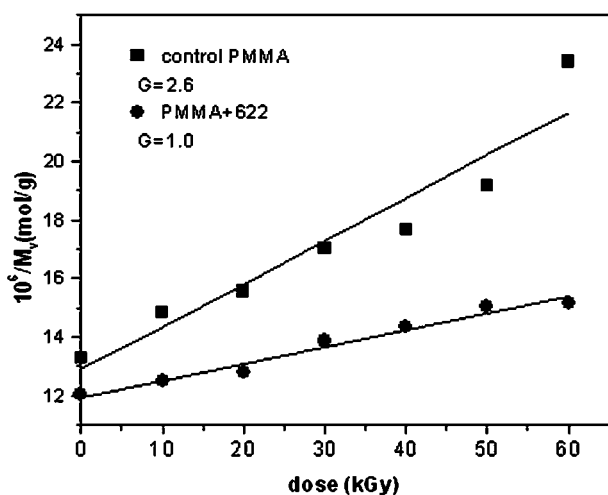


Figure 1 Reciprocal of molecular weight of PMMA and PMMA + 622 as a function of the irradiation dose.

ther eq. (4) n is the order of reaction, for many pyrolysis processes, $n = 1$, i.e., first order reaction and χ represents extent of sample being degraded:

$$\chi = (W_0 - W_t) \alpha (W_0 - W_f) \quad (5)$$

where W_0 , W_t , and W_f are the weight of sample before degradation, during and after complete degradation, respectively. On integrating eq. (4) and after several assumptions for the integral function, several methods for evaluation of thermokinetic parameters (A and E_a) from a single thermogravimetric experiment have been developed by many scientists.¹⁷⁻¹⁹ According to the expression obtained by Broido for $n = 1$.¹⁷ The eq. (6) shows the relation between χ and the reciprocal of T .

$$\log[-\log(1 - \chi)] = -(E_a/2.303R)[(1/\alpha T) + K] \quad (6)$$

In this method a linear relationship should be observed between $\log[-\log(1 - \chi)]$ and $1/\alpha T$ with a slope of $-E_a/2.303R$. The activation energy was calculated by regression analysis.

RESULTS AND DISCUSSION

Viscometric and spectroscopic analysis

Comparison of viscometric results obtained before and after irradiation showed a decrease in M_v values on irradiated samples. These results could be explained by the occurrence of main chain scission, whose mechanism is well known.¹⁴ The variation of the reciprocal M_v values with irradiation dose for control PMMA and PMMA + 622 are given in Figure 1. As shown in Figure 1, the G values found for the control PMMA and PMMA + 622 were 2.6 and 1.0 scissions/100 eV, respectively, at dose interval of

0–60 kGy. The P value calculated is 0.61. This result represents 61% of reduction in yield of chain scissions in PMMA macromolecules containing Tinuvin 622. At 30 kGy dose (near to sterilization dose), we calculated $DI = 2.8$ for control PMMA and $DI = 0.8$ for PMMA + 622. These data represent a decrease of 71% in scissions per original molecule of PMMA + 622.

High-speed processing machines exert shear forces on melt polymer that can lead to local overheating. Therefore, most industrial processes, i.e., injection molding or extrusion provoke a decreasing in molecular weight due to thermal degradation. In Figure 1 can be observed that the reciprocal molar weight of PMMA + 622 is smaller than unirradiated control PMMA samples. These results suggest that control PMMA undergoes more thermal degradation in industrial process than PMMA + 622. Results about thermal degradation of PMMA were examined in this study.

FTIR spectra of control PMMA and PMMA + 622, both unirradiated and irradiated at 60 kGy dose showed similar patterns (Fig. 2). These results indicate the absence of formation of new bonds between Tinuvin 622 and PMMA matrix. Specific band shifts

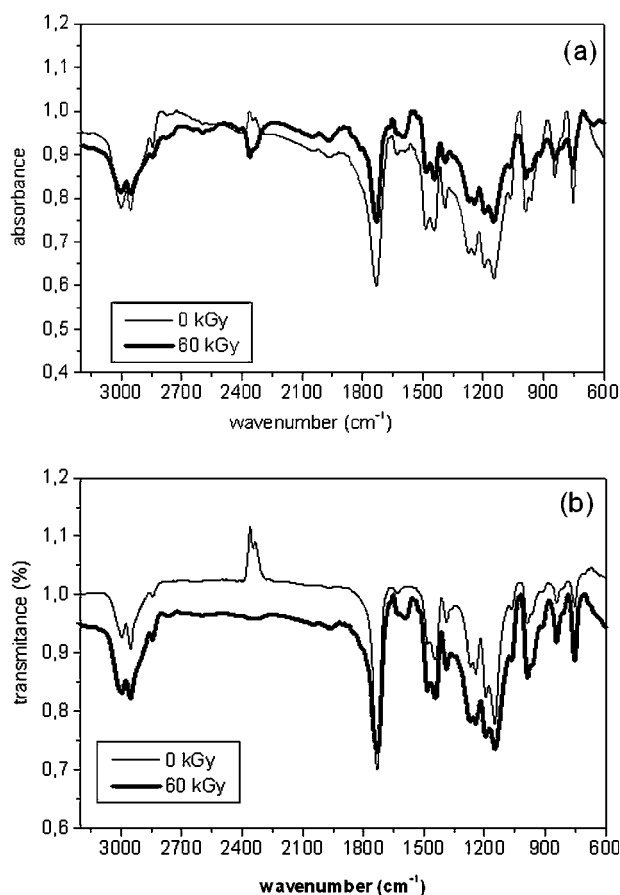


Figure 2 FTIR spectra of (a) control PMMA and (b) PMMA + 622.

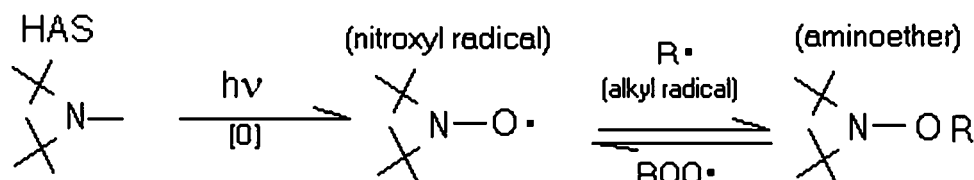
TABLE I
Carbonyl Index (CI) of Control PMMA and PMMA+622

| Dose (kGy) | Control PMMA | PMMA+622 |
|------------|--------------|----------|
| 0 | 5.20 | 5.25 |
| 60 | 1.53 | 2.31 |

are additional methods were required in order follow degradation process quantitatively. Stretching vibrations peak from C=O at pendant carboxymethyl group appeared at 1734 cm^{-1} . This peak decreases in irradiated samples. Previous study showed similar results for gamma irradiated PMMA.²⁰ The major gaseous products formed from PMMA under gamma irradiation are methyl formate, methane and methanol (derived from methyl), CO and CO₂ along with many other products.^{21,22} Formation of gaseous products involved from pendant methyl groups should always be reflected in the changes in intensity of carbonyl bands in FTIR spectra. The carbonyl index (CI) was determined by the ratio A_{1734}/A_{753} , where A_{1734} is the intensity of C=O stretch band and A_{753} is the CH₂ rocking vibration that does not change with irradiation. These data showed decrease of carbonyl index in both samples (Table I), however the PMMA + 622 present lower CI decrease than control PMMA.

The Scheme 1 is generally accepted to explain the aspects of the chemistry mechanism of HAS action to inhibit polymer photo-oxidation.^{23,24} This scheme was used in this work to guide a strategy to assess Tinuvin 622 action in radiolytic stabilization of PMMA. According to this scheme, the tetramethylpiperidine moiety, which is the basic structure of HAS, is initially oxidized to produce a nitroxyl radical by gamma irradiation. The nitroxyl radical acts as a scavenger of the radical originating from the irradiation of polymer chain substrate to form an alkylated aminoether. From the aminoether, the nitroxyl radical is regenerated through quenching another peroxy radical produced by oxidation of the polymer chain. Thus the nitroxyl radicals could regenerate many times through the chain reaction before their depletion.

FTIR and M_v data show good gamma radiation stabilizing effect of Tinuvin 622 in PMMA matrix, suggesting the scavenger of radicals originating from radiolysis process.



Scheme 1 Typical photo-stabilizing action of HAS in the polymer system.

Figure 3(a) shows the ¹H NMR spectrum of commercial PMMA. Main peaks at 0.81 and 0.99 ppm have been assigned to proton of α-methyl group, the peaks 1.79 and 3.58 have been assigned to protons of methylene and pendent methyl ester group, respectively. Peaks at 5.4 and 6.14 ppm [insert on Fig. 3(a)] have been assigned to the methylene proton of the vinylidene end groups, which is formed through free-radical polymerization of PMMA.^{9,10} Identical peaks were found for irradiated PMMA [Fig. 3(b)], however the peaks assigned to the methylene proton of the vinylidene groups disappeared in irradiated sample [insert on 3(b)]. The carbon-carbon double bonds are particularly susceptible to damage by gamma radiation. Similar results were obtained for PMMA + 622.

Thermogravimetric analysis

The Figure 3(a) showed that the polymer in study is a double bond terminated PMMA (PMMA—CH=CH₂). PMMA—CH=CH₂ undergoes easy β homolytic cleavage at the terminal double bond, leading to thermal degradation. However, previous study⁹ demonstrated that thermal degradation of PMMA—CH=CH₂ occurs by an efficient chain-transfer process in which the end group reacts with a radical to form an active end, which can depolymerize.

TGA thermograms of control PMMA and PMMA + 622 are shown in Figures 4 and 5, respectively, along with derivative curves. Relative thermal stability of the control PMMA and PMMA + 622 samples was evaluated by comparison of the decomposition temperature at onset (T_s) and at 50% of decomposition (T_{50}) by TG analysis and maximum thermal degradation (T_{mx}) by DTG curves. The TG analysis results are listed in Table II. Higher values of T_s , T_{50} , and T_{mx} indicate thermal stability of the polymers. Unirradiated and irradiated samples were found to undergo a single step of decomposition in temperature range of 290–380°C for control PMMA [Fig. 4(a,b)] and irradiated PMMA + 622 [Fig. 5(b)], whereas the decomposition temperature range of 300–400°C was found for unirradiated PMMA + 622 [Fig. 5(a)]. The derivative curves of control PMMA degradation showed a small shoulder at peak temperature of 334 and 330°C in unirradiated and irradiated

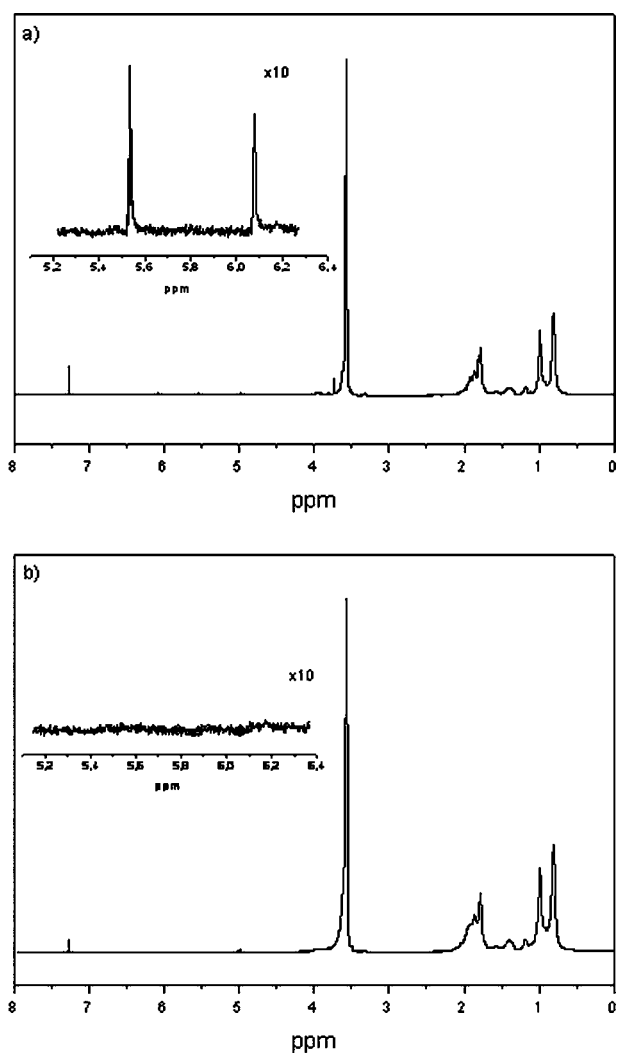


Figure 3 ^1H NMR spectra of control PMMA a) unirradiated and b) irradiated.

ated samples, respectively. However the peak increasing its intensity in irradiated sample [Fig. 5(b)]. Since PMMA sample used in this study was a commercial material, it is expected to contain some impurities such as unreacted initiator, monomer, ultraviolet absorber, etc. These impurities can play an important role in thermal degradation of PMMA as demonstrated by Hirata et al.¹¹

In the control PMMA, the T_{mx} and T_{50} peaks for irradiated samples occurred at lower temperature than unirradiated sample (Table II). We infer that the decrease in T_{50} and T_{mx} may be due to the consumption of Tinuvin 622 during exposure to ionizing radiation.

T_{50} of PMMA + 622 is 32°C higher than T_{50} of control PMMA in unirradiated samples. Similarly the T_{mx} of decomposition peak is about 367°C for PMMA + 622 and 325°C for control samples in DTG curve [Figs. 4(a) and 5(a)]. These results show an increase of 42°C in T_{mx} of PMMA + 622 and shows

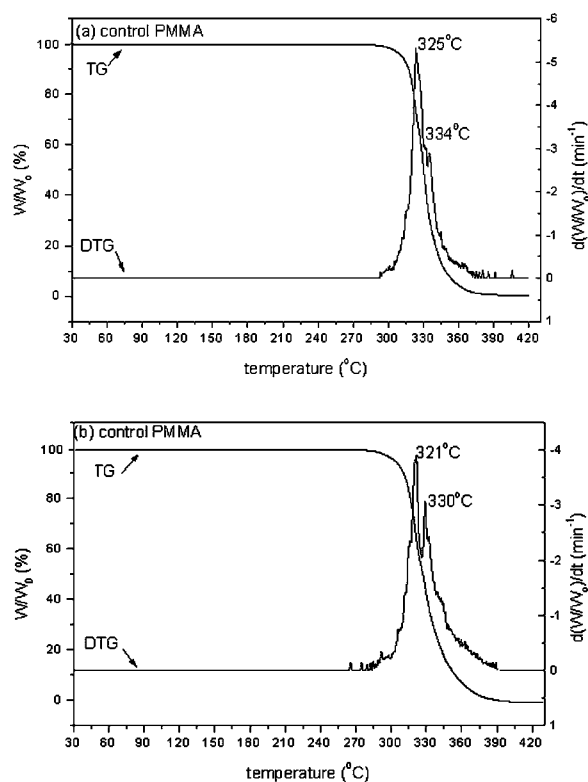


Figure 4 TG and DTG curves of control PMMA (a) unirradiated and (b) irradiated at 60-kGy dose.

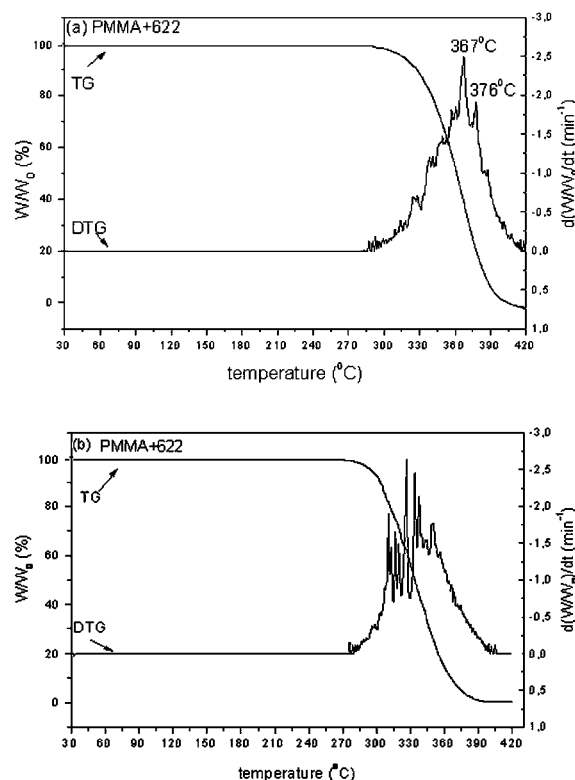


Figure 5 TG and DTG curves of PMMA + 622 (a) unirradiated and (b) irradiated at 60-kGy dose.

TABLE II
The Thermal Degradation Temperatures of Control PMMA and PMMA+622

| Dose (kGy) | Control PMMA | | | PMMA+622 | | |
|------------|--------------|---------------|---------------|------------|---------------|---------------|
| | T_s (°C) | T_{50} (°C) | T_{mx} (°C) | T_s (°C) | T_{50} (°C) | T_{mx} (°C) |
| 0 | 290 | 330 | 325 | 300 | 362 | 367 |
| 60 | 290 | 326 | 321 | 290 | 328 | 322 |

that thermal stability of PMMA was improved by Tinuvin 622. On the other hand the DTG curves of PMMA + 622 irradiated at 60-kGy dose [Fig. 5(b)] show consecutive peaks between 290 and 400°C. T_{mx} of decomposition peak was not identifiable. This result is probably due to a complex degradation mechanism triggered by the radiation effects in the system.

The efficiency of Tinuvin 622 in thermal stabilization of unirradiated PMMA can be determined by inhibition of radical processes in the system by additive. Stabilization of the degradation products by the Tinuvin 622 is also possible.

TGA was also used to investigate the activation energy corresponding to the weight loss initiated by random scissions.¹⁷ Table II shows the unirradiated samples present higher thermal stability than irradiated sample. Thus the activation energy for irradiated samples is not discussed in this study. Using the Figure 6 the value activation energy for control PMMA was calculated to be 165 kJ/mol, this energy increased to 225 kJ/mol when Tinuvin 622 was added to PMMA (temperature range of 290–380°C). These results represent higher thermal resistance of PMMA + 622 compared to PMMA without Tinuvin 622. Previously reported values of activation energies for PMMA corresponding to same event (random scissions) were 207 kJ/mol,²⁵ 230 kJ/mol,²⁶ and 275 kJ/mol.²⁷ The value calculated in our study for control PMMA is lower compared to the previ-

ous values probably due to the effect of impurities in the commercial samples used.

CONCLUSIONS

The viscosity analysis and carbonyl index calculated from FTIR spectra suggest that Tinuvin 622 (0.3% wt/wt) protects PMMA against radiolysis by free radical scavenging. The G values (scissions/100 eV) were 2.6 for control PMMA and 1.0 for PMMA + 622 at dose range of 0–60 kGy. These results represent 61% of reduction in yield of chain scissions in PMMA matrix. NMR ¹H results showed the influence of gamma irradiation on methylene proton of the vinylidene end groups of control PMMA.

Comparison of TG and DTG curves of control PMMA with PMMA + 622 shows that Tinuvin 622 increased the PMMA stability by increasing 32°C the temperature for 50% of decomposition and 42°C in maximum temperature of the weight loss. However, no significant difference was observed in both irradiated system. This works demonstrates that the activation energy for PMMA + 622 is 60 kJ/mol higher than control PMMA (unirradiated samples).

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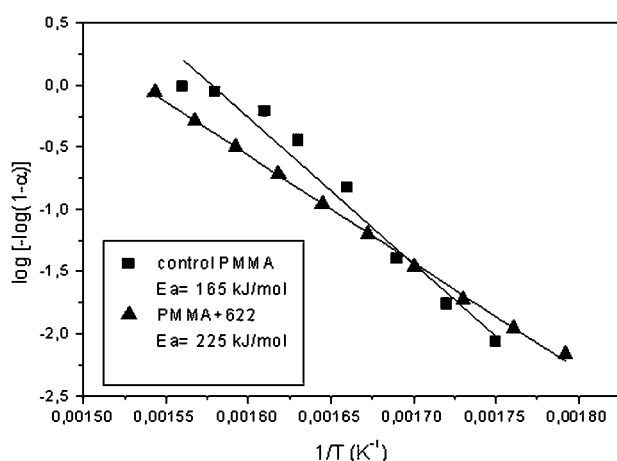


Figure 6 Plot of $\log [-\log(1 - \chi)]$ versus $1/T$ of unirradiated samples.

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