

Influence of γ -Irradiation on Poly(methyl methacrylate)

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ABSTRACT: Poly(methyl methacrylate) (PMMA) was γ -irradiated (5–20 kGy) by a ^{137}Cs source at room temperature in air. The changes in the molecular structure attributed to γ -irradiation were studied by mechanical testing (flexure and hardness), size-exclusion chromatography, differential scanning calorimetry, thermal gravimetric analysis, and both Fourier transform infrared and solution ^{13}C -NMR spectroscopy. Scanning electron microscopy was used to investigate the influence of the dose of γ rays on the fracture behavior of PMMA. The experimental results confirm that the PMMA degradation process involves chain scission. It was also observed that PMMA presents a brittle fracture mechanism and modifications in the color, becoming yellowish. The mechanical property curves show a similar pattern when the γ -radiation dose increases. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 886–895, 2002

Key words: poly(methyl methacrylate); γ -irradiation; radiation damage; yellowing

INTRODUCTION

Poly(methyl methacrylate) (PMMA) has been widely employed in industrial and domestic appliances since it was commercialized in the beginning of the 1930s. PMMA may be produced and formed into rigid bodies showing attractive features, excellent transparency ($\sim 92\%$), good mechanical properties, and high resistance to atmospheric agents.¹ It has been used for aeronautical and medical applications as well as in the electronics and microelectronics industries.^{2,3}

A huge source of natural radiation on Earth is cosmic rays, which are of great concern because of their incidence on aircraft, passengers, and crews. The sterilization of medical supplies is now being mainly performed by γ -irradiation. When PMMA is exposed to radiation damage, its chemical and physical properties are modified. This polymer may be taken as a model for chain scission without simultaneous crosslinking after exposure to ionizing radiations.⁴

In the present work, samples of commercial PMMA, after irradiation in air with low doses of γ rays, were evaluated through mechanical and physicochemical methods. The fracture behavior of the material was investigated by scanning electron microscopy (SEM). PMMA showed modifications in the mechanical properties and a brittle fracture. These results are presented and discussed, to correlate the experimental data with the molecular structure.

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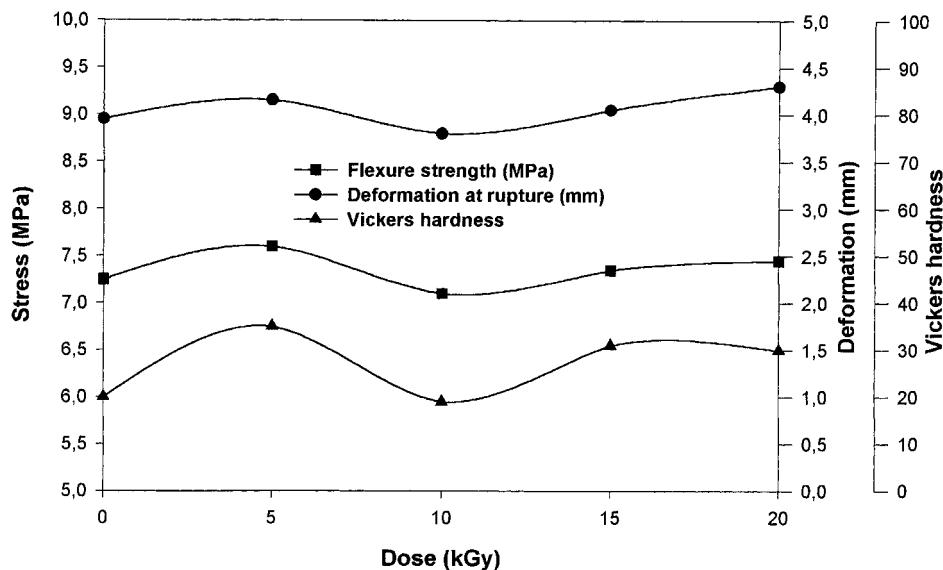


Figure 1 Variation of the mechanical properties of PMMA with the radiation dose.

EXPERIMENTAL

The 5-mm-thick PMMA plate used in this work is a commercial product, for application in aircraft radomes. This material, which was supplied according to international aeronautical quality standards, was manufactured by thermoforming. Additional information about the production conditions was not obtained. The exposure of samples to γ -radiation was performed in experimental equipment with a ^{137}Cs radiation source. The specimens were irradiated to 5, 10, 15, and 20 kGy (0.5, 1.0, 1.5, and 2.0 Mrad), at a dose rate of 2.5 kGy/h, in air at room temperature. The effect of γ -radiation on the polymer samples was investigated by mechanical testing (flexure and hardness), differential scanning calorimetry (DSC), thermogravimetric analyses (TGA), size-exclusion chromatography (SEC), Fourier transform infrared spectroscopy (FTIR), and solution ^{13}C -NMR spectroscopy as well as scanning electron microscopy (SEM).

Three-point flexure tests were carried out according to ASTM D 790 standard⁵ in a model DL2000 Emic universal-testing machine with a crosshead speed of 1.30 mm/min (Emic Ltda., S. José dos Pinhais, PR (Brazil)), at room temperature. For each sample group five specimens were tested (dimensions of $60 \times 10 \times 5$ mm, machined from the plate). The flexure resistance limit and the deformation at rupture were determined.

The Vickers hardness measurements were performed in a Micromet 2003 Buehler digital micro-

hardness tester (Buehler Ltd., Lake Bluff, IL), before and after irradiation. The indenting load was 10 g. For each sample group at least 10 indentations were made at different parts of the specimens and an average value was computed.

The molecular weight was determined using a 600E Waters HPLC (Waters Associates, Milford, MA), equipped with a refractive index and four Waters Ultrastaygel columns (10^5 , 10^4 , 10^3 , and 500 \AA), with 1,2,4-trichloro-benzene as solvent at 135°C as mobile phase (0.5 mL/min). Polystyrene was used as a standard for calibration purposes.

FTIR spectroscopy measurements in the range $4000\text{--}400 \text{ cm}^{-1}$ were carried out using a 1720x Perkin-Elmer spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) and cast films from CHCl_3 solutions as samples. The spectra were

Table I Molecular Weights and Molecular Weight Distribution of PMMA, Before and After γ -Irradiation

Dose (kGy)	Average Molecular Weight		Polydispersity \bar{M}_w/\bar{M}_n
	\bar{M}_n	\bar{M}_w	
0	105,800	922,500	8.7
5	114,500	468,300	4.1
10	96,700	305,200	3.2
15	75,100	218,400	2.9
20	70,300	192,600	2.7

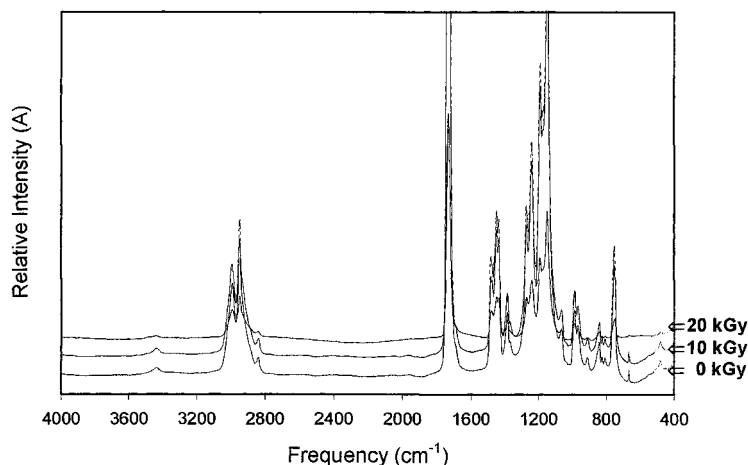


Figure 2 Infrared spectra (MIR) of PMMA, before and after irradiation.

obtained at a 2 cm^{-1} resolution, 20 scans, and processed by a Perkin-Elmer IR data manager (IRDM).

Calorimetric data were determined with a DSC-7 Perkin-Elmer apparatus equipped with TAS-7 software and a Perkin-Elmer PE-7700 professional computer. The equipment was calibrated with indium ($T_m = 156.6^\circ\text{C}$ and $\Delta H_f = 6.8\text{ cal/g}$) as standard. Samples of about 10 mg were sealed in aluminum pans and were submitted to a repeated heating/cooling cycle varying from 30 to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. The glass-transition temperature

(T_g) was determined according to the ASTM D 3418 standard.⁶

TGA analyses were carried out using a Perkin-Elmer TGA-7 thermobalance, the accuracy of which was within 0.1%, and a chromel-alumel thermocouple precision of about 2°C . The thermocouple calibration was performed with alumel ($T_c = 163^\circ\text{C}$), nickel ($T_c = 354^\circ\text{C}$), and perkallo ($T_c = 596^\circ\text{C}$) standards. The samples weighing about 3 mg were heated from 30 to 600°C with a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere, at a flow rate of $33\text{ mm}^3/\text{min}$ for the sample and $60\text{ mm}^3/\text{min}$ for the furnace.

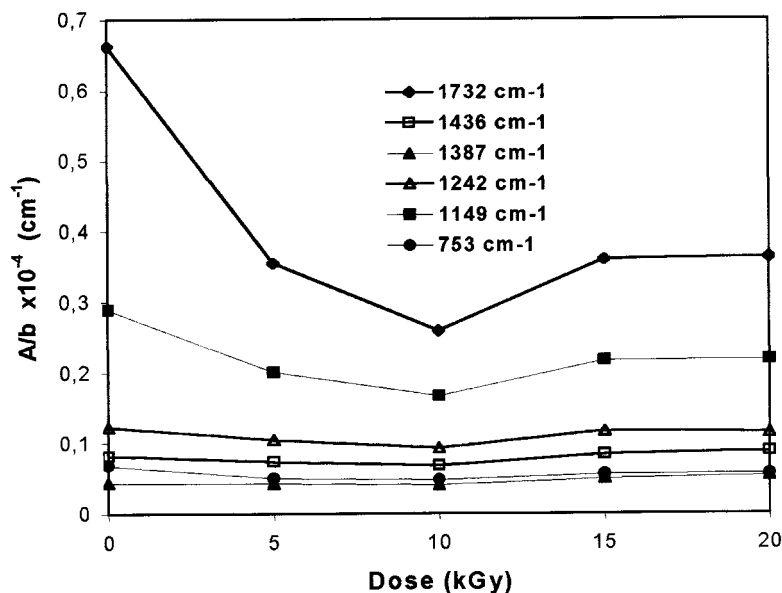


Figure 3 Relationship between the ratio intensity/film thickness (A/b) of the typical absorption bands and the radiation dose.

Table II Typical Infrared Spectral Bands for PMMA

Absorption Band	Frequency (cm ⁻¹)
C=O stretching	1732
CH ₂ deformation	1436
CH ₃ symmetrical deformation	1387
C—C(C=O)—O and O—C—C—	1272, 1242
CH ₃ in —CH ₂ —CH(CH ₃)—CH ₂ —; —C—O	1149
CH ₂ rocking vibration	753

From Silverstein et al.⁸ and Colthup et al.⁹

The solution ¹³C-NMR analyses were carried out on a Varian Mercury 300 spectrometer (Varian Associates, Palo Alto, CA) operating at 75.4 MHz for ¹³C and the spectra were recorded at ambient probe temperature. Samples were prepared in CDCl₃ solvent at 20% (w/w) concentration. The ¹³C determinations were performed with a spectral width of 18 kHz over an acquisition time (pulse) of 8.1 μ s (90°) and a relaxation delay time of 20 s.

The failure mechanisms of PMMA were studied by direct observation of the topography of flexure fracture cross section of the specimens after testing. The fracture surfaces were examined with the naked eye and by means of a JSM 5800LV JEOL scanning electron microscope (JEOL, Peabody, MA). Before SEM examination,

the surfaces were sputter-coated with a thin layer of gold in a vacuum chamber.

RESULTS AND DISCUSSION

Figure 1 shows flexure strength, deformation at rupture, and hardness of PMMA after irradiation. There is a slight variation in the values, with a bimodal shape of the curves and a minimum for the 10-kGy dose, indicating modifications in the polymer molecules.

The number-average molecular weight (\bar{M}_n), the weight-average molecular weight (\bar{M}_w), and the molecular weight distribution, calculated from SEC curves of the PMMA samples, are presented in Table I. Comparison of the data from unexposed samples with data obtained after γ -irradiation shows a decrease in the molecular weight values and in the molecular weight distribution. These results could be explained by the occurrence of chain scission.⁷ Essentially, as indicated by the molecular weight distribution, the γ -irradiation transforms the PMMA into a lower molecular weight material, whose chain dissimilarities were not significantly different.

The infrared spectra of PMMA showed the same pattern in all samples. Figure 2 presents the FTIR spectra of PMMA, before and after irradiation, that were very similar. This result indicates the absence of strong chemical structural changes in the samples. The more pronounced

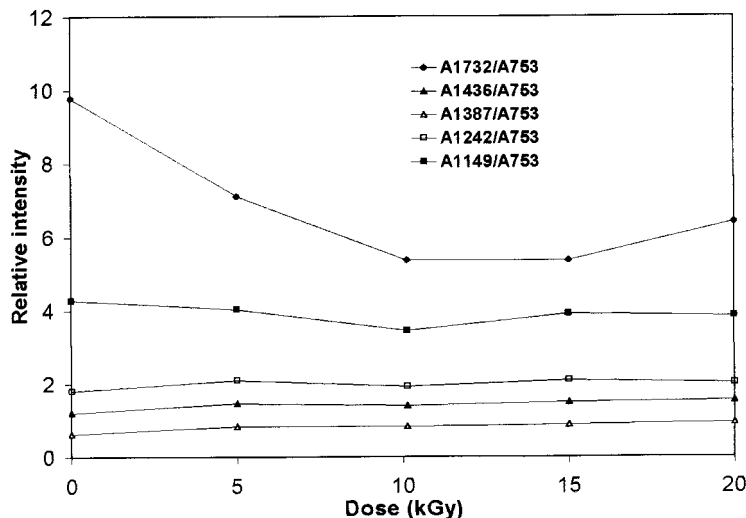


Figure 4 Relative absorbance of typical PMMA absorptions as a function of the radiation dose.

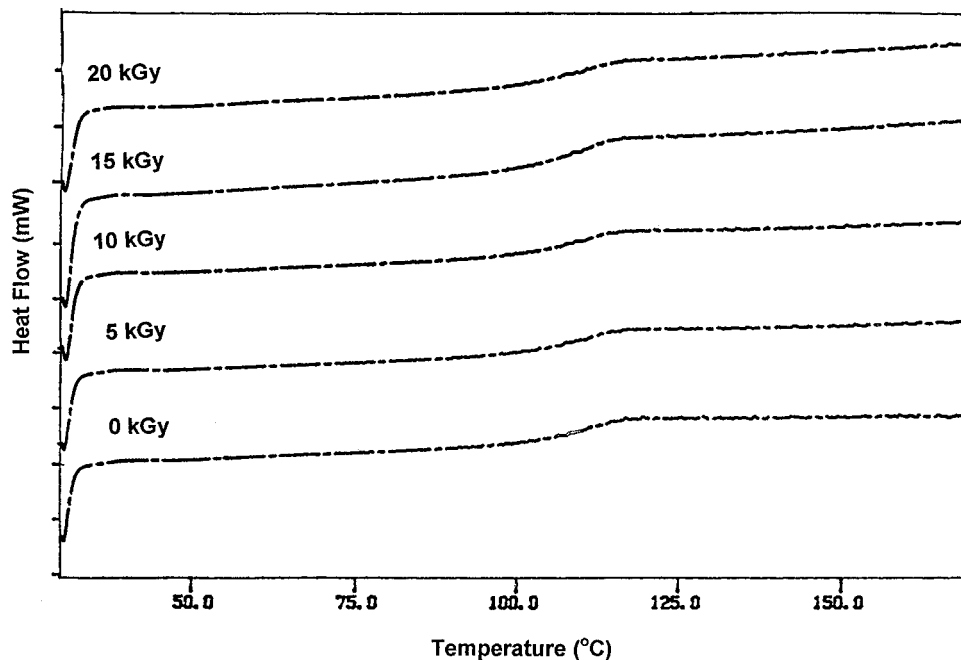


Figure 5 Calorimetrics curves of PMMA, before and after irradiation.

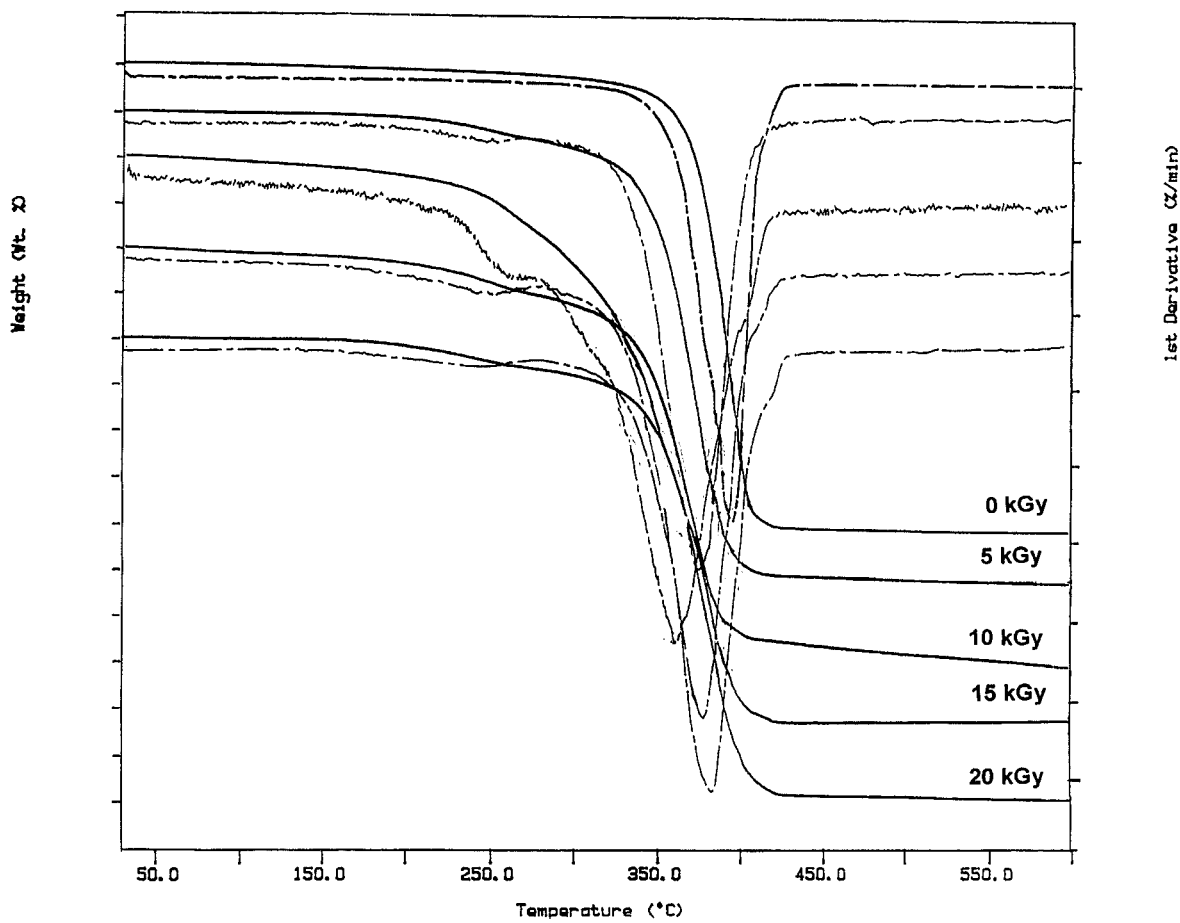
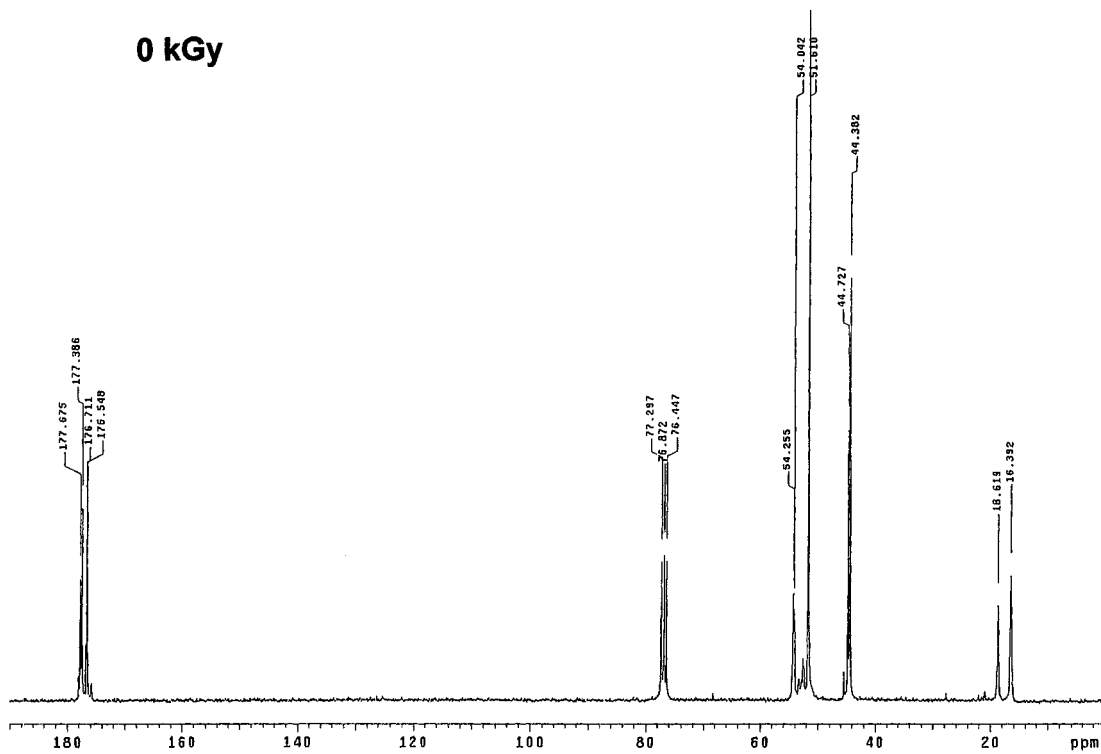
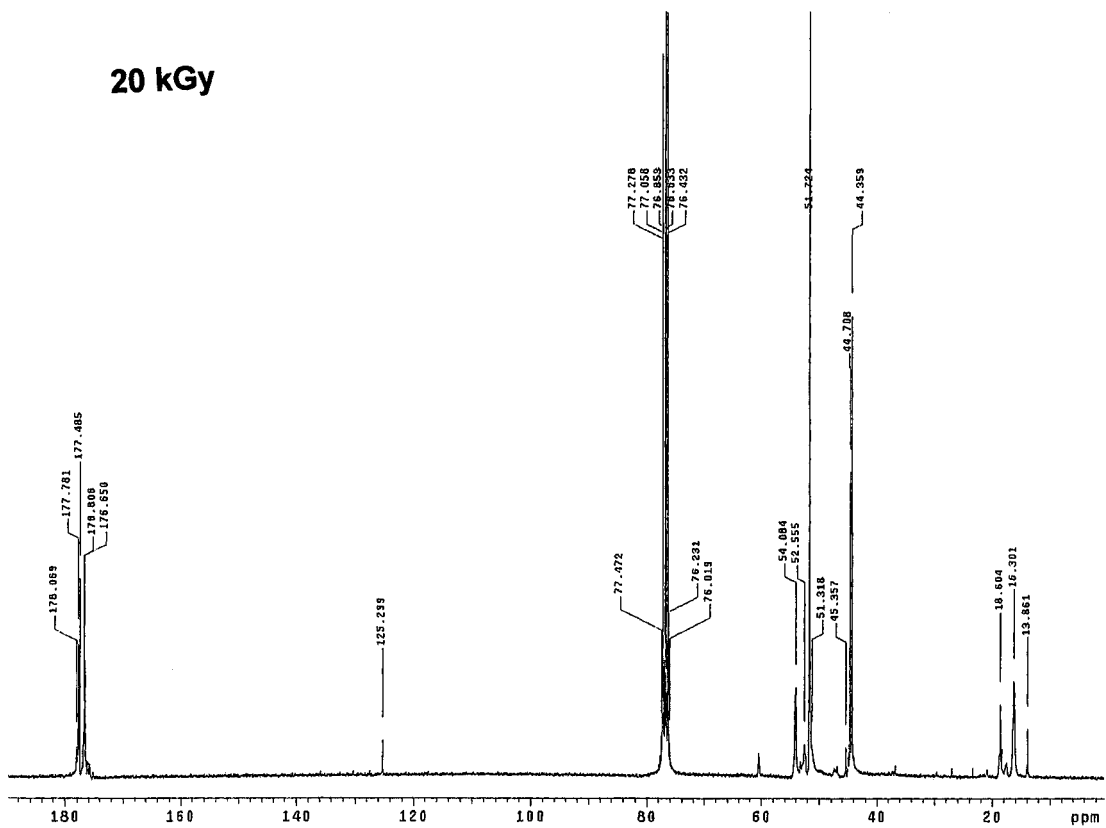


Figure 6 TGA curves of PMMA, before and after irradiation.



(a)



(b)

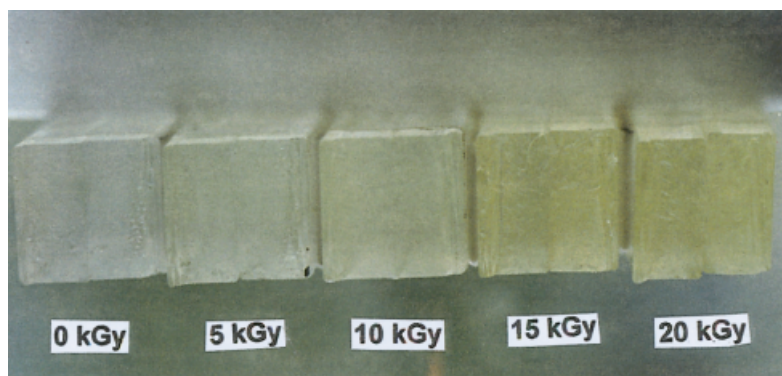


Figure 8 Macroscopic aspects of flexure fracture surfaces, before and after irradiation.

modifications occur at lower radiation doses, as shown by the variation of the intensity of typical absorption bands. However, the effect of irradiation on mechanical properties and molecular weight suggested a more detailed evaluation of the spectra. The spectra were obtained using cast films as samples, and a thickness correction was needed for purposes of intensity comparison. Thus the ratio intensity/film thickness (A/b) of the typical absorption bands was used. The results, depicted in Figure 3, indicate a similar behavior for the majority of the selected absorption bands. The chosen absorptions are listed in Table II.^{8,9} Figure 3 shows that the intensity of the carbonyl absorption decreases with the increasing dose up to 10 kGy. The higher doses promoted an increase of this absorption and achieved a plateau of sorts. Similar behavior is followed by the absorption at 1149 cm^{-1} .⁹ The remaining characteristic absorptions presented small changes that cannot be considered significant. The data presented the best fitting when the relative absorbance was plotted as a function of the radiation dose (Fig. 4). The absorption used as a reference was the CH_2 rocking vibration at 753 cm^{-1} . It is observed that the intensity of the decreasing carbonyl absorption achieves a minimum and increases at doses higher than 15 kGy. The band at 1149 cm^{-1} presented small changes and the other characteristic absorptions, which presented the same pattern, did not show any significant effect from the irradiation. These results support the hypothesis of chain scission followed by oxidation processes. The degradation process seems to occur as long as

the PMMA samples are exposed to γ -radiation, as indicated by the variation of the intensity of the carbonyl group absorption: the degradation mechanism proposed in the literature shows that main-chain scission occurs with the evolution of CO and CO_2 .¹⁰ The presence of unsaturated linkages is also described.¹⁰ Afterward, the oxidation process is started. The modifications in the degradation mechanism influence the mechanical behavior of the samples, as observed in the flexure and hardness tests.

Typical DSC curves obtained from the PMMA samples, before and after irradiation, are depicted in Figure 5, where it is observed that there was no significant variation in the T_g 's of nonirradiated and irradiated materials. However, the samples irradiated with doses of 10 kGy and higher show a small increase in T_g , indicating the possibility of a double-bond production in the chain ends attributed to higher material radiolysis.^{11,12}

Figure 6 shows TGA curves, where differences in the degradation profiles may be observed. Table III presents the degradation (onset and peak) temperatures, before and after irradiation, calculated from TGA curves. The data show, in the second step, a marked minimum of the degradation temperatures in the material irradiated with the 10-kGy dose. These data indicate that the γ -irradiation produces a structural degradation in the material and that the chain scission occurs predominantly after a 10-kGy radiation dose. This result is in accordance with the infrared data.

Figure 7 shows typical ^{13}C -NMR spectra of PMMA, before and after irradiation. It is impor-

Figure 7 Typical ^{13}C -NMR spectra of PMMA, before and after irradiation: (a) non-irradiated (0 kGy); (b) irradiated with 20 kGy.

Table III Degradation Temperatures of PMMA as a Function of Radiation Dose

Dose (kGy)	Onset Temperature (°C)		Peak Temperature (°C)	
	Step 1	Step 2	Step 1	Step 2
0	—	373	—	395
5	212	350	248	375
10	234	318	262	371
15	219	350	240	376
20	196	356	241	382

tant to note the occurrence of two signals that did not belong to PMMA, the first located at about 60 ppm (attributed to $\text{CH}_3\text{—O}$) and the other one at 125 ppm (attributed to the olefinic methylene). To evaluate the degradation process of PMMA, variations in the carbonyl group microstructure were determined. The PMMA is an amorphous polymer composed of small segments of ordered sequences known as isotactic (mm), heterotactic (mr), and syndiotactic (rr). From the spectra, the splitting carbonyl group shows triads and pentades. The assignments and quantification of different configuration sequences allows us to evaluate the changes caused in the molecular mobility resulting from the irradiation process. The analyses of the NMR spectra allow us to verify that the γ -irradiation modifies the microstructure. These changes are listed in Table IV, indicating that the PMMA degradation is random, generating products such as monomers and oligomers. It can be concluded that the PMMA is degraded by scission of the side-group links at the main chain and at the methoxy group. These results confirm the observed IR test data.

Figure 8 presents a macroscopic view of fracture surfaces on the flexure specimens. The naked-eye observation shows that the transparency of the polymer was not significantly modified by the irradiation, although showing a color change from white to brownish. PMMA, which is transparent and colorless in its as-received state, presents a progressive yellowing that is more prominent with the increase of the radiation dose, principally for doses higher than 10 kGy. This behavior indicates the formation of a chromatic group, possibly by the introduction of conjugation to the carbonyl groups of the chain.¹³ This may be ascribed to the formation of a double bond and

oxidation and harmonizes with the results of the infrared spectroscopy.

Typical microphotographs of the fracture surfaces of flexure specimens are shown in Figure 9. As expected, the PMMA samples present, before and after irradiation, a brittle fracture behavior with the characteristic features of flat surfaces and sharp edges.¹⁴ One observes the existence of three areas that are significantly different: (1) an initial zone, with a mirrorlike polish, corresponding to the beginning of the crack; (2) a diffuse, mistlike region, characterized by a low increase in the superficial roughness; and (3) an irregular hackle region, with plain and rough areas. At higher magnifications differences in the morphology of the hackle region can be distinguished: an increase in the radiation dose produces a sensitive increase in its roughness. It was verified that the samples irradiated with the largest doses (15 and 20 kGy) presented larger plastic areas (Fig. 10), characterized by greater toughness. This is related to the ability of the material to slow down or arrest the crack; the higher radiation doses increase the amount of shorter chains in the irradiated material, which facilitates the disentanglement of the chains and favors microvoid formation in the rupture. SEM features are in accordance with GPC results and support the increase in the observed deformation values in the flexural strength determinations.

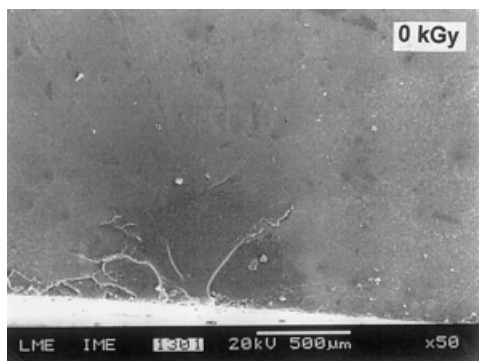
The work continues at our laboratories.

CONCLUSIONS

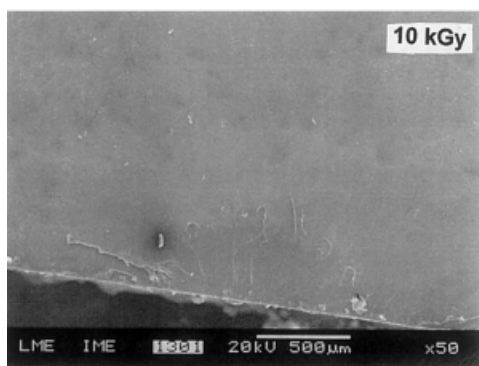
The present analysis indicates that PMMA irradiated with γ rays in air presents chain scission and oxidative degradation. This modifies the mo-

Table IV Determination of the Triads from the Carbonyl Group, Before and After Irradiation by ^{13}C -NMR

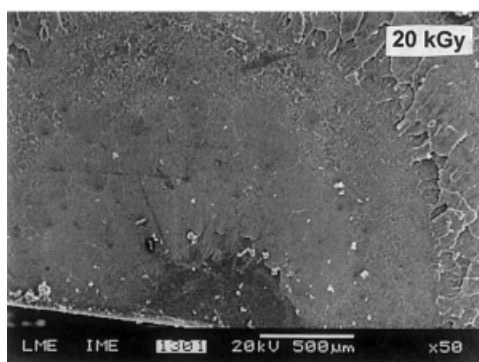
Dose (kGy)	Configurational Sequences (%)		
	mm	mr	rr
0	7.3	25.8	40.8
5	13.7	34.6	51.4
10	10.1	34.6	54.4
15	14.9	34.1	49.1
20	10.1	34.7	54.3



(a)



(b)



(c)

Figure 9 SEM micrographs of flexure fracture surfaces: (a) nonirradiated (0 kGy); (b) irradiated with 10 kGy; (c) irradiated with 20 kGy. Crack propagation from bottom to top.

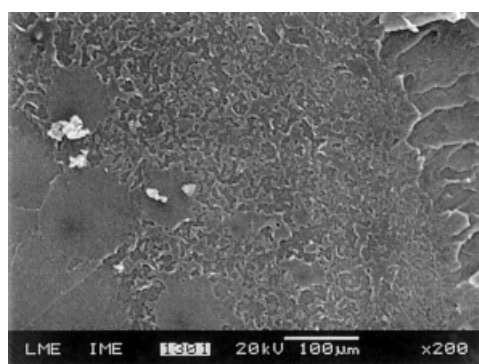
lecular structure of the material and may change its mechanical properties.

The principal conclusions are as follows:

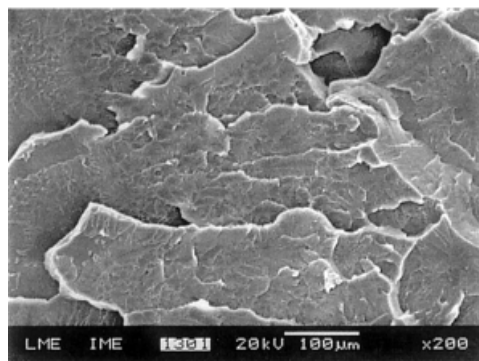
1. PMMA radiolysis occurs as a result of the scission of the main chain, as indicated by the decrease in the molecular weight.

2. The γ -irradiation does not change the stiffness of PMMA but produces modifications in the flexure properties, with a tendency to improve the deformation in the rupture resulting from the chain scission.
3. Relationships were observed between the features of fracture surfaces and the mechanical properties in the flexure testing; higher radiation doses might modify the brittle behavior of PMMA, leading to a more ductile fracture mechanism.

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(a)



(b)

Figure 10 SEM micrographs of fracture surfaces of flexure specimens irradiated with 20 kGy: (a) diffuse region; (b) hackle region. Crack propagation from left to right.

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