

## Gamma irradiation of food packaging materials: an NMR study

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### Abstract

The effects of  $\gamma$  irradiation on polymers used in food packaging have been studied by NMR. In order to assess the presence of a threshold dose for an observable effect, the whole range of 1–100 kGy was investigated. Polystyrene, poly-butadiene, styrene–acrylonitrile, high-impact polystyrene and acrylonitrile–butadiene–styrene were studied before and after the  $\gamma$  irradiation treatment and in the presence or in the absence of antioxidants and stabilizers. In the absence of stabilizers, the effect of  $\gamma$  irradiation on polystyrene is negligible even when operating at high doses. In contrast, the role of antioxidants and stabilizers is crucial in poly-butadiene and butadiene-containing copolymers. High-resolution NMR, dynamic mechanical analysis, impact analysis and gel permeation chromatography performed on irradiated polystyrene samples do not show any detectable effect, confirming polystyrene as an ideal polymer for food packaging use. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polymers;  $\gamma$  Irradiation; NMR

### 1. Introduction

Polymeric materials are strongly affected by ionizing radiation. Our work concerns the very specific and developing field dedicated to the study of materials employed in irradiated food packaging. We apply a very versatile tool, the NMR spectroscopy, to study both aromatic and aliphatic polymers irradiated with low values of  $\gamma$  ray dose ( $D$ ).

Food irradiation treatment is highly efficient in avoiding undesirable phenomena such as sprouting and contamination by poisoning bacteria. With the aim of decreasing the occurrence of food diseases and delaying the growth and ripening of fruits and vegetables, radiation is used to kill cells and to alter the enzyme activities in food. Depending on the desired effect, the dose of food irradiation is associated with a typical range: from few kGy (sprout inhibition) up to tens of kGy (sterilization) [1,2]. In 1980, the FAO, IAEA and WHO committees recognized all foods irradiated up to an overall average dose of 10 kGy as safe.

Most foods are subjected to irradiation treatment after they have been packaged. Hence, in order to reveal possible interactions between the packaging, the food and the radiation, it becomes crucial to study the effects of radiation on

both the food and the packaging separately. The irradiation of glass packaging is known to cause only the unpleasant aesthetic effect of brown tinting upon treatment while plastic packaging may suffer damages that compromise its proper functionality as a container.

High-energy irradiation was reported to affect the integrity of plastic materials, which become ineffective against microbiological contaminants. In addition, the irradiation process was observed to induce plastic materials to release small particles into foods thus altering the food quality itself [3]. Radiation is known to affect polymer properties. The grafting of monomers onto polymer chains may induce the formation of new classes of material. Moreover, radiation effects could be responsible for polymer degradation, oligomer formation and subsequent cross-linking. However, depending on the application, the induction of a certain amount of cross-link may even improve the performance of the materials, raising the temperature of the fusion point and the resistance to several solvents.

Based on different values of the absorbed dose, radiation effects on polymers may be classified as follows:

1. Scission and/or cross-linking of the polymer chains with a consequent molecular weight decrease and/or increase.
2. Occurrence of chemical reactions leading to small volatile products and, eventually, organic radicals which are potential contaminants of the packaged foods.

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Table 1  
Glass transition temperature ( $T_g$ ) of the styrene component, density and tensile modulus of PS, SAN, HIPS and ABS are reported

Materials	$T_g$ (°C)	Density (kg/m <sup>3</sup> )	Tensile modulus (MPa)
PS	103	1050	3200–3300
SAN	103	1070	3500
HIPS	103	1040	1700–1800
ABS	109	1040	2600–2700

3. Occurrence of structural modifications of polymer chains, such as changes in the number of unsaturations, presence of charged units and so on.

It has been shown that aromatic polymers have a greater resistance to radiation than aliphatic chains since the phenyl rings provide both an intra- and inter-molecular protective effect. In this regard, there is much interest in the quantification of different levels of radiation protection by different aromatic structures [4,5].

Polymers commonly used in food packaging often contain low molecular weight compounds such as monomers and oligomers, residues from the polymerization process, and additives such as antioxidants, light stabilizers and plasticizers which are added to improve the polymer stability and performance. The lower the molecular weight of the compounds, the greater their mobility and therefore, the probability that they migrate into the food. Furthermore, the irradiation process may not only affect the polymeric material itself, but may also cause the degradation of additives and the migration of by-products into the food; experimental results point to a greater tendency towards migration for the products deriving from the degradation of stabilizers than for the intact stabilizers themselves [6].

The identification and measurement of radiation-induced changes in polymers are carried out by a number of experimental techniques, such as pulse radiolysis of radicals and ionic intermediates, gas chromatography and mass analysis of volatile products, dynamic mechanical measurements and some spectroscopic techniques such as ESR, NMR and IR spectroscopy [7–9].

Indirect measurements such as changes in molecular weight, elastic modulus, soluble fraction, etc. reveal the presence of both cross-linking and scission in irradiated polymers. However, they do not give information about the chemistry of such processes.

NMR spectroscopy enables us to obtain this kind of information and seems to be one of the most versatile methods as well. The highest resolution can be achieved in solution. In fact, <sup>1</sup>H and <sup>13</sup>C NMR spectra in solution allow the observation of minor components such as oligomers and additives [10]. Solid state NMR techniques are also useful in the study of the insoluble part of irradiated polymers [11]. On solid samples, pulsed low-resolution <sup>1</sup>H NMR studies can give precise measurements of  $T_1$  (spin-relaxation time),  $T_{1\rho}$  (spin-lattice relaxation time in the rotating frame) and  $T_2$

(spin-spin relaxation time) [12]. These parameters, in turn, are strongly correlated to polymer mobility and its physical state [13]. Thus, information regarding changes in polymer molecular motions occurring upon  $\gamma$  irradiation can be obtained [14].

Dynamic mechanical analysis was also used to investigate possible changes in the molecular architecture of irradiated samples. In fact, it is known that, at least for high irradiation doses, the dynamic shear modulus  $G'$  of irradiated samples increases [15]. This effect, possibly due to cross-linking, is quoted in the literature for polystyrene samples exposed to a  $\gamma$  irradiation dose which is about four orders of magnitude higher than the  $\gamma$  irradiation dose considered here.

In this paper, a combination of NMR, dynamic mechanical and chromatography techniques is applied to the study of  $\gamma$  irradiation effects on the polymeric materials commonly used in food packaging such as polystyrene (PS), poly-butadiene (PB), styrene-acrylonitrile (SAN), high-impact polystyrene (HIPS) and acrylonitrile butadiene styrene copolymer (ABS).

## 2. Materials and methods

Polymers were commercial products obtained with bulk polymerization and supplied by EniChem. Polystyrene and styrene-acrylonitrile copolymers (acrylonitrile content 25% (w/w)) were obtained by direct thermal polymerization of monomers. Poly-butadiene samples contain  $\approx$ 40% *cis*-1,4 and 5% 1,2.

High-impact polystyrene and acrylonitrile-butadiene-styrene copolymers were obtained with a similar procedure, the only difference being the presence of poly-butadiene during the polymerization process. The presence of PB (10% (w/w)) causes the growing chains of PS (or SAN) to graft directly on PB chains. Typical properties of the studied polymers are reported in Table 1.

### 2.1. Polymer purification procedure

To remove commercial additives, residual monomers and oligomers, samples were purified according to a solvent/insolvent precipitation procedure. About 1 g of polymer was dissolved in 30 ml of CHCl<sub>3</sub> and the solution was magnetically stirred for 2 h. The solution was then slowly added to 300 ml of CH<sub>3</sub>CH<sub>2</sub>OH in drops under continued stirring. The polymer was precipitated, filtered and dried under vacuum at 40°C for about 10 h.

### 2.2. Sample irradiation

The powdered samples were irradiated in glass ampoules using a <sup>60</sup>Co  $\gamma$ -cell, the average dose being 6 kGy/h. Absorbed doses  $D$  ranged from 1 to 100 kGy: in order to assess the presence of a threshold dose for an observable effect, we studied the irradiation effects at low

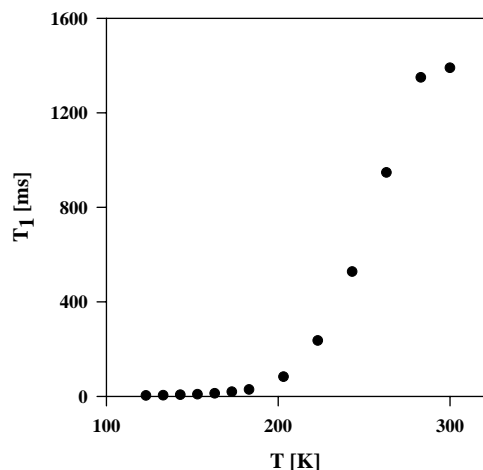


Fig. 1.  $^1\text{H}$  spin-lattice relaxation time measured at 75 MHz as a function of the temperature. Sample: purified PS.

doses (1, 2 and 5 kGy up to the food irradiation approved limit of 10 kGy), and at high doses (30, 50 and 100 kGy).

### 2.3. NMR relaxation

Pulsed low-resolution  $^1\text{H}$  NMR measurements were performed at 75 MHz on a commercial spectrometer “Spin-master” (Stelar, Mede (PV), Italy) equipped with a variable temperature unit controller. The samples were contained in standard 5 mm NMR tubes. To ensure a suitable oxygen source [16], a large glass cylinder was sealed onto the top of each tube. The height of the sample, which was finely powdered and slightly compressed in the NMR tube, was carefully kept within the coil (about 4 mm). Since most polymers are highly hygroscopic, the NMR tubes were filled with dry air just before each measurement.

$T_1$  spin-lattice relaxation times were measured by the aperiodic saturation recovery sequence (APSR) consisting of a train of 15 ( $\pi/2$ ) pulses spaced out in an aperiodic way. The sequence was run according to a multi-block multi-scan

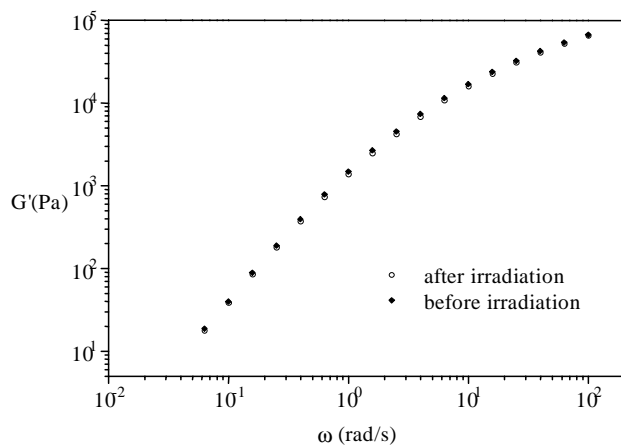


Fig. 2. Angular frequency dependence of the dynamic shear modulus  $G'$  of PS before and after  $\gamma$  irradiation.

Table 2

Data from unnotched Charpy tests are reported in  $\text{kJ/m}^2$

Sample	( $\text{kJ/m}^2$ )
Not irradiated PS	$13.09 \pm 2.54$
$D = 10$ kGy	$11.51 \pm 2.17$
$D = 30$ kGy	$10.12 \pm 1.34$

procedure. In each experiment, the number of blocks, corresponding to the number of different  $\tau$  delays, was at least 64 for single exponential decays and 128 for multiple exponential decays. The mean value of the first 12 points after the dead time was calculated for each block to evaluate the magnetization of the fast relaxing PS component. In turn, the mean value of the points from 50 to 150 was calculated to evaluate the long relaxing PB component.

$T_2$  spin-spin relaxation times were measured by performing a Carr-Purcell-Meiboom-Gill (CPMG) sequence. In this sequence the application of a  $\pi/2$  pulse was followed by a  $\pi$  pulse after a variable delay  $\tau$ :  $(\pi/2 - \tau_i - \pi)_n$ ,  $i = 512$ , the number of echoes that result in a multi-exponential decay of 512 experimental points. The starting  $\tau/2$  delay value was 25  $\mu\text{s}$  and the incremental delay  $\Delta\tau$  was 50  $\mu\text{s}$ . The signal to noise ratio was improved by a multiple scan procedure repeated  $n = 2^{10}$  number of times. The full phase cycle was performed on the full acquisition set.

### 2.4. Data analysis

APSR experiments lead to an equation of the type:

$$M = \sum_i A_i \exp(-t/T_{1i}) + A_0,$$

where  $i = 1, \dots, N$  and  $N$  is the number of different  $T_i$  with relative spin densities  $A_i$ ; while  $A_0$  is the value of the magnetization after a single  $\pi/2$  pulse.

CPMG experiments lead to an equation of the type:

$$M = \sum_i A_i \exp(-t/T_{2i}) + C_0,$$

where  $C_0$  is the mean value of the experimental noise.

These equations were fitted with the commercial computer program “Stefit” [17], which uses a “Simplex” algorithm [18]. The experimental deviation was compared with the calculated one and their compatibility tested to a 99%

Table 3

Molecular weight distributions measured by GPC are reported for nonirradiated and irradiated PS samples

Sample	$M_n$ (Daltons)	$M_w$ (Daltons)	$M_w/M_n$
Not irradiated PS	126 000	238 000	1.88
$D = 1$ kGy	128 000	232 000	1.81
$D = 2$ kGy	130 000	235 000	1.82
$D = 10$ kGy	126 000	234 000	1.86
$D = 30$ kGy	125 000	236 000	1.89

Table 4

As a function of the  $\gamma$  irradiation dose, the amount of monomer and low molecular weight compounds measured in PS samples by gas chromatography, is reported in ppm (parts per million)

	Not irradiated PS	$D = 1$ kGy	$D = 2$ kGy	$D = 10$ kGy	$D = 30$ kGy
<i>cis</i> -1,2-Diphenyl cyclobutane	13	11	12	10	8
2,4-Diphenyl 1 butene	52	47	53	50	50
<i>trans</i> -1,2-Diphenyl cyclobutane	137	136	136	128	125
2,4,6-Triphenyl 1 esene	613	576	645	563	560
(1-Phenylethyl)-1,2,3,4-tetrahydronaphthalene	5000	4600	5200	5000	4800
1-Isopropylbenzene	8	10	7	8	9
Styrene	158	233	210	184	183

confidence level according to an  $F$  distribution. The presence of a comparable number of negative and positive deviations was also checked. The number of sign changes of the ordered experimental points was evaluated and compared with a binomial distribution: only distributions within 99% confidence level were accepted.

The reported data are to be considered within the following limits: single exponential, error within 2%; multiple exponential, error on the longest  $T_i$  value and on the other  $T_i$  values within 2 and 5%, respectively; error on  $A_i$  values less than 10% for each component.

### 2.5. High-resolution solid state NMR

Solid state  $^{13}\text{C}$  CP MAS NMR spectra were performed at 50.33 MHz on a Bruker AC-200 spectrometer, equipped with an HP amplifier  $^1\text{H}$  200 MHz, 120 W CW and with a pulse amplifier M3205. The samples were finely powdered and packed into 4 mm zirconia rotors and sealed with Kel-F caps.

The single pulse excitation (SPE) method was applied to obtain  $^{13}\text{C}$  MAS NMR spectra. The relaxation delay was 20 s. The spinning rate was 8 KHz. Spectra were obtained with 1024 words in the time domain, zero filled and Fourier

transformed with a size of 2048 words.  $^1\text{H}$  MAS NMR spectra at 200.13 MHz of ABS samples were also performed to observe the quite sharp resonances resulting from the PB component [19].

### 2.6. NMR in solution

$^1\text{H}$  NMR spectra were carried out on a Bruker AMX 600 spectrometer operating at 600.13 MHz on proton. The samples were prepared by dissolving 10 mg of powdered polymer in 1 ml of  $\text{CDCl}_3$ . The fraction of irradiated PB which was insoluble in  $\text{CDCl}_3$  was dried and then dissolved in  $\text{C}_2\text{D}_2\text{Cl}_4$  (1 mg/ml) at high temperature.  $^1\text{H}$  NMR spectra were run at 343 K.

### 2.7. Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements were performed in the shear mode with a Rheometrics mechanical spectrometer (RMS) model 800 under  $\text{N}_2$  atmosphere. The samples were compression molded at  $190^\circ\text{C}$  to fit the RMS tools. The shear modulus  $G'$  was measured in the linear viscoelastic region using 25 mm parallel plate geometry (gaps ranging between 1 and 2 mm), at  $220^\circ\text{C}$  in the frequency range between 0.1 and 100 rad/s. Strain sweeps has been previously performed to ensure the linearity of the viscoelastic response.

### 2.8. Impact analysis

The impact analysis were performed according to the ISO 179 1eA standard on unnotched specimens.

### 2.9. Gel permeation chromatography (GPC)

Molecular weight distributions were determined by size exclusion chromatography (SEC); the experimental apparatus included a Waters 590 pump, a Waters WISP 712 injector and a bench of four  $300 \times 7.6$  i.d. mm Phenogel columns ( $5 \mu\text{m}$  particle diameter,  $10^6$ – $10^5$ – $10^4$ – $10^3$  Å pore size).

The detection was assured by a Waters 410 differential refractive index detector and by a Waters 440 UV detector ( $\lambda = 254$  nm). Tetrahydrofuran (THF-Merck) was used as a solvent; it was previously purified from stabilizer and on-line degassed by a ERMA degasser. The elutions were

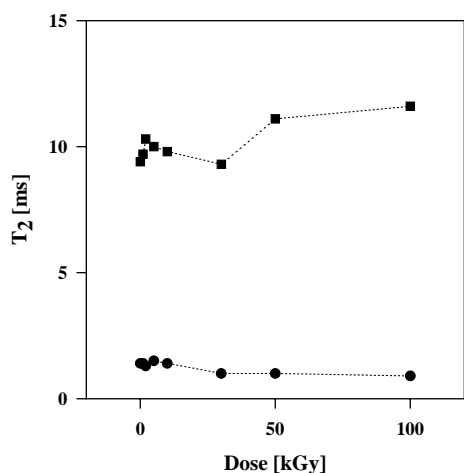


Fig. 3. Correlation between  $^1\text{H}$  spin–spin relaxation time and the  $\gamma$  irradiation dose. Sample: PB;  $T = 300$  K. Circles refers to the fast  $T_2$  component, squares refers to the slow one.

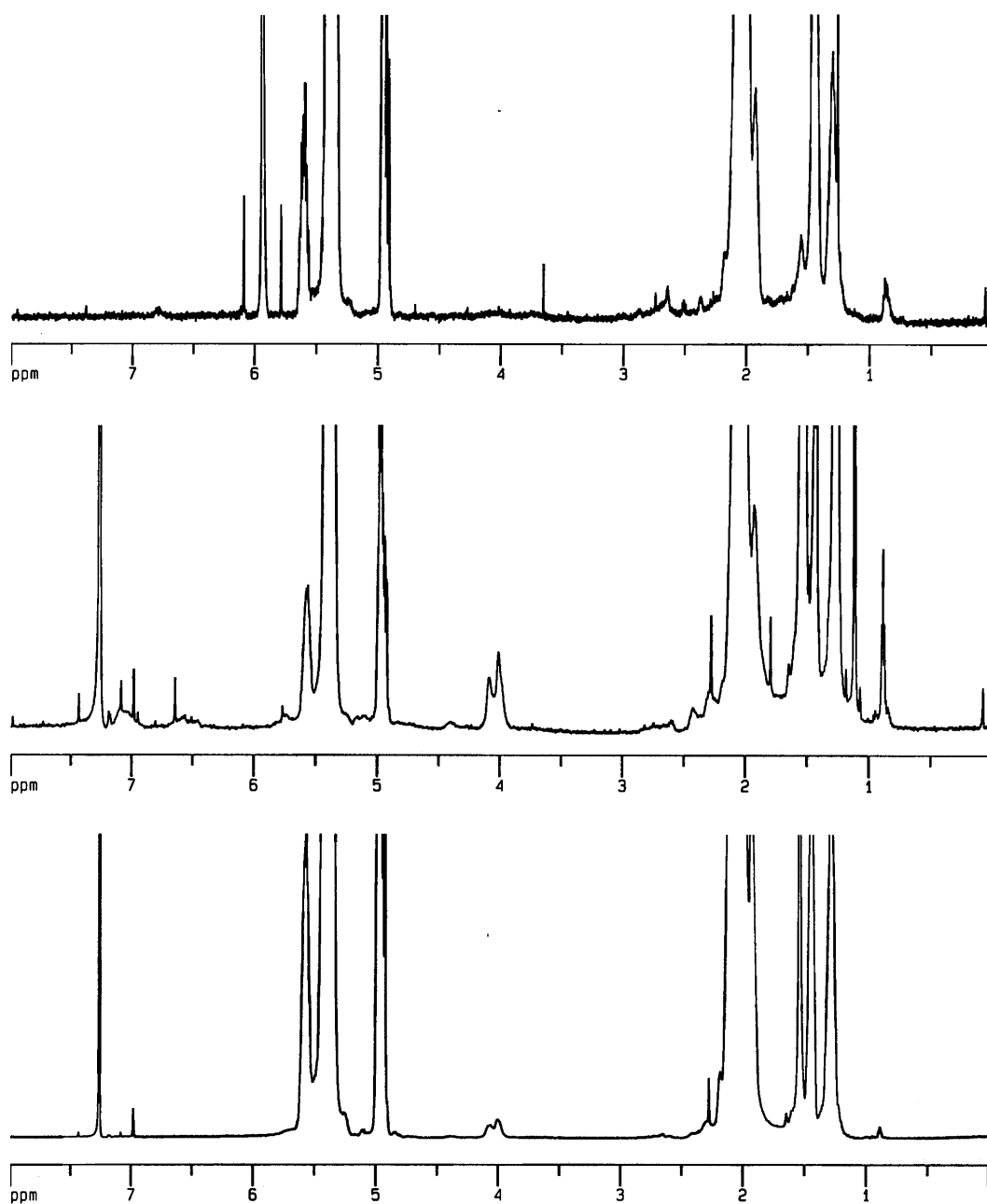


Fig. 4.  $^1\text{H}$  NMR spectra at 600.13 MHz for: (bottom) nonirradiated PB in  $\text{CDCl}_3$ ,  $T = 300$  K; (middle) soluble fraction of irradiated PB in  $\text{CDCl}_3$ ,  $D = 100$  kGy,  $T = 300$  K; (top) insoluble fraction of irradiated PB in  $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $D = 100$  kGy,  $T = 343$  K.

performed at room temperature at a flow of 1 ml/min injecting 150  $\mu\text{l}$  of 0.15% (w/v) THF solutions. A broad standard calibration, obtained with an NBS 706 PS standard, was applied for the calculation of molecular weight distribution. Data collection, calibration and calculation were performed with Millenium 2.15 analysis software.

#### 2.10. Gas chromatography (GC)

Gas chromatographic analysis were carried out using a capillary GC column with Carbowax phase, 0.53 diameter, 30 m length and 3  $\mu\text{m}$  of film thickness.

### 3. Results and discussion

#### 3.1. Polystyrene

It is well known that aromatic polymers are able to selectively absorb oxygen [20]. The paramagnetic oxygen acts as a strong contrast agent modulating the spin–lattice relaxation values [21,22]. Since the oxygen absorption is in turn modulated by the presence of cross-links or oligomers, the relaxometric method becomes extremely powerful and can be used for the detection of small effects, which are not observable with any other method.

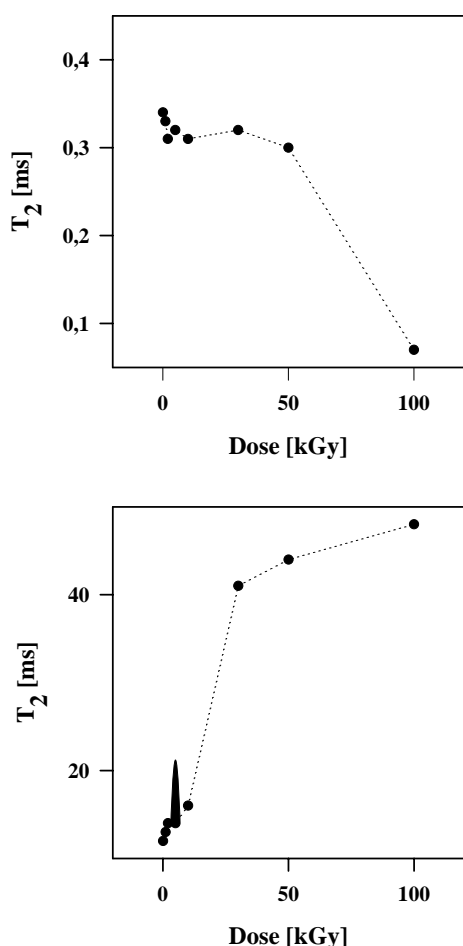


Fig. 5. Correlation between  $^1\text{H}$  spin–spin relaxation time and the  $\gamma$  irradiation dose. Sample: purified HIPS;  $T = 300\text{ K}$ . Collected data show a three exponential behavior.  $T_2$  values are relative to the fast (top) and the slow (bottom) relaxing components, respectively. The medium component is quite insensitive to  $\gamma$  irradiation.

Proton  $T_1$  spin–lattice relaxation times were measured for polystyrene at 75 MHz as a function of the temperature, see Fig. 1. The data reported in the figure refer to a purified fully amorphous polystyrene sample. According to previous observations [23], a marked shortening of  $T_1$  values is observed by decreasing the temperature. However, only one  $T_1$  component is measured in the whole range of temperature indicating that the spin diffusion process between aliphatic and aromatic protons is always active [24].

Purified polystyrene samples were irradiated with the following  $D$  values of  $\gamma$  ray: 1, 2, 5, 10, 30, 50 and 100 kGy.  $T_1$  relaxation times were measured as a function of the temperature for the set of irradiated samples and compared with the corresponding values of those that were not irradiated. A slight lengthening of  $T_1$  measured at very low temperature,  $T < 260\text{ K}$ , was only observed for samples irradiated with high doses ( $50\text{ kGy} < D < 100\text{ kGy}$ ). While,  $^1\text{H}$  NMR spectra at 600.13 MHz of purified polystyrene samples before and

after irradiation do not show any detectable differences even at high doses.

The same approach was performed to study commercial polystyrene containing Irgafos P-EPQ as an anti-oxidant additive. In this case, no appreciable difference was detected as a function of the dose in either  $T_1$  relaxation times or high-resolution solid state  $^{13}\text{C}$  MAS spectra or in  $^1\text{H}$  NMR spectra recorded at 600.13 MHz in solution.

These findings were also confirmed by dynamic mechanical measurements, see Fig. 2. In this figure the angular frequency dependence of the dynamic shear modulus  $G'$  of polystyrene before and after  $\gamma$  ray exposure is reported. No increase of  $G'$  for the 100 kGy irradiated sample is observed, indicating that this  $\gamma$  irradiation dose does not affect the molecular structure [15].

Upon  $\gamma$  irradiation, no evidence of real damage to materials was found either during mechanical tests (Table 2) or during GPC analysis (Table 3). In order to check for chemical effects of  $\gamma$  irradiation, gas chromatographic analysis was carried out on both nonirradiated and irradiated PS. The reported data show both a small increase of the styrene monomer and a slight degradation of cyclic dimers (cyclobutanes) for the irradiated samples (see Table 4).

These results suggest that polystyrene is quite stable; this property is due to the presence of aromatic groups able to absorb and dissipate the penetrating energy [25].

### 3.2. Styrene–acrylonitrile copolymers

Styrene–acrylonitrile copolymers do not contain any anti-oxidant additives. A content of about 1% (w/w) of oligomers and volatile compounds is normally present. Furthermore, SAN is highly hydrophilic. Again, we treated the commercial samples and the purified SAN copolymers separately.

In a previous work [26], we reported data for SAN commercial samples. By a combination of relaxometric methods, we performed an accurate description of minor transitions occurring at low temperature. In SAN copolymers the selective absorption of small molecules such as paramagnetic oxygen and water allows for the precise measurement of a second order transition due to the phenyl ring libration [26].

The  $T_1$  of SAN was measured at 81 MHz. By lowering the temperature, a minimum is present at  $\approx 240\text{ K}$  in the presence of oxygen. As usual, when the amount of oxygen is high enough, the spin diffusion process is ineffective and the aromatic protons of styrene show a  $T_1$  relaxation time much shorter ( $\approx 30\text{ ms}$ ) than the value ( $\approx 500\text{ ms}$ ) of backbone protons.

At very low temperature, ( $T < 200\text{ K}$ ), the  $T_1$  relaxation times measured in all irradiated SAN samples are slightly longer than those measured in nonirradiated samples. However, this effect is so small that, presently, we are unable to establish a clear correlation between the observed lengthening of  $T_1$  and the irradiation doses. After  $\gamma$  irradiation, no

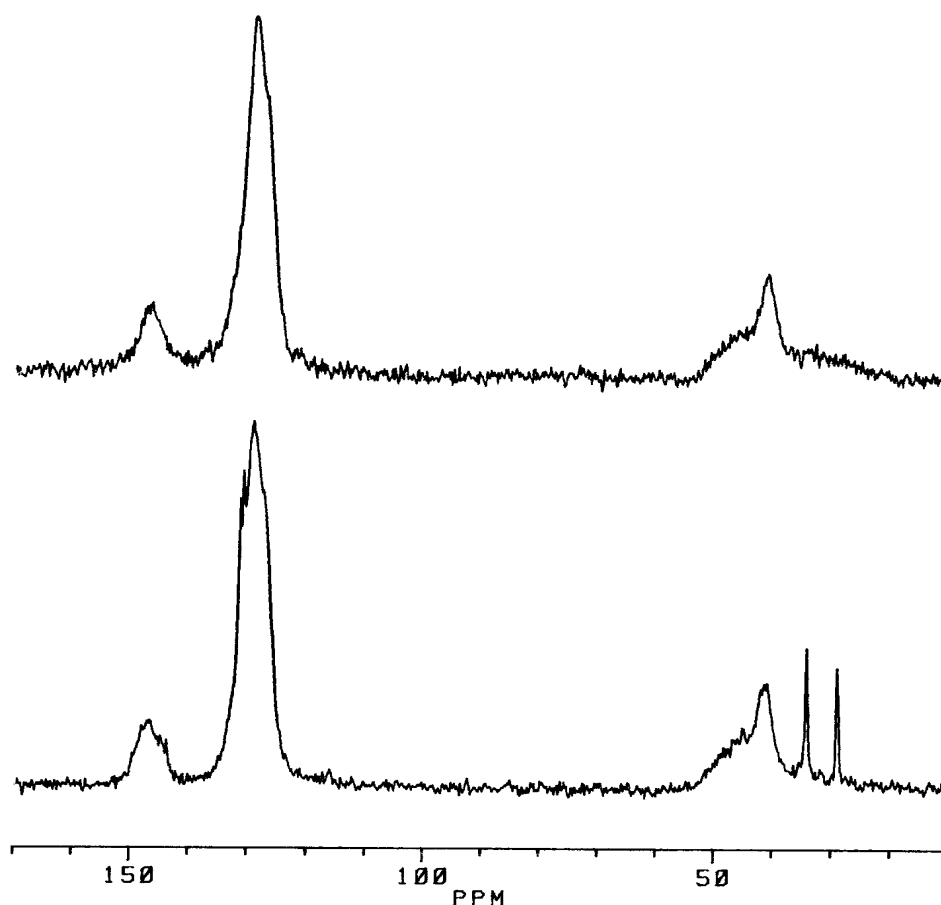


Fig. 6.  $^{13}\text{C}$  CP MAS spectra recorded at 50.33 MHz for purified HIPS: (bottom) nonirradiated sample,  $T = 300\text{ K}$ ; (top)  $D = 100\text{ kGy}$ ,  $T = 300\text{ K}$ .

significant effect can be observed by either high-resolution  $^1\text{H}$  NMR methods in solution or  $^{13}\text{C}$  NMR performed in the solid state.

### 3.3. Poly-butadiene

Many polymers used in food packaging contain variable amounts of poly-butadiene. Thus, the effect of  $\gamma$  irradiation on poly-butadiene and diene containing polymers, was also investigated.

These polymers undergo cross-linking very easily both between adjacent chains and separated domains [25]. Furthermore, since these polymers show great instability when exposed to light and air, we performed experiments on poly-butadiene samples containing a proper amount of anti-oxidant additives as stabilizers.

The main effect of radiation on these polymers is the degradation and/or the formation of intermolecular bonds (cross-linking). This latter effect leads to an increase in both the average molecular weight and in their intrinsic viscosity. At a comparatively high-absorbed dose, a fraction of the cross-linked polymer forms a gel that is insoluble in most organic solvents [25]. Cross-linking was first studied in detail in polyethylene [27]. As a result of radiation induced

cross-linking, polyethylene undergoes considerable changes. Upon treatment with high doses, from many kGy to several MGy, reduced solubility in organic solvents and a higher melting point are found. As a consequence, changes in polymer flexibility are observed.

At room temperature poly-butadiene is well above its  $T_g$ , so that its proton resonance appears sharp allowing  $T_2$  relaxation time measurements. Due to the presence of different domains, two  $T_2$  components are observed, see Fig. 3. A full simulation of the experimental data shows that the ratio of the spin density of the short  $T_2$  component and the spin density of the long  $T_2$  component is 1:1. Hence, a possible attribution might be due to the presence of domains that are quite stiff (characterized by a short  $T_2$ ) and more mobile domains (characterized by a long  $T_2$ ). The domain composition might reflect heterogeneity in the ratio *cis*-1,4 ( $\approx 40\%$ )/*trans*-1,4 ( $\approx 55\%$ ), or it might be due to cross-links originally present in the polymer. Both the short and the long  $T_2$  components seem to be rather insensitive to the  $\gamma$  irradiation process.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in the solid state show the same trend. Thus, even if the  $\gamma$  irradiation dose is high ( $\approx 100\text{ kGy}$ ), the  $^{13}\text{C}$  MAS spectrum at 50.33 MHz is much similar to the spectrum obtained on nonirradiated

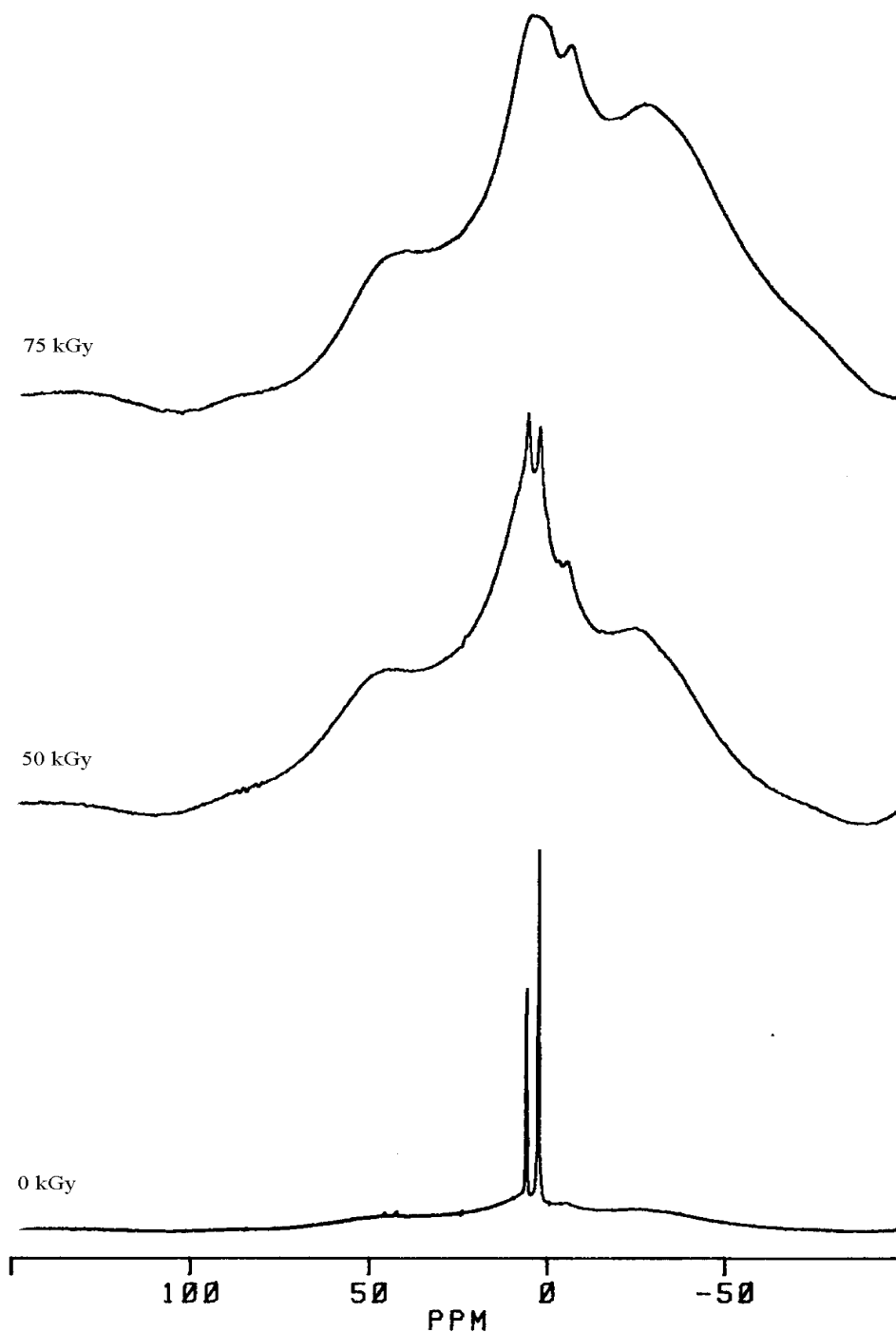


Fig. 7.  $^1\text{H}$  MAS spectra recorded at 200.13 MHz for purified ABS. Data were collected at 300 K as a function of the irradiation dose: (bottom) nonirradiated sample; (middle)  $D = 50$  kGy; (top)  $D = 100$  kGy.

poly-butadiene samples. The key method in this case is  $^1\text{H}$  NMR performed in solution. In fact  $^1\text{H}$  NMR spectra in solution show  $\gamma$  irradiation-induced effects, see Fig. 4.

The irradiation of poly-butadiene results in two main effects: the cut of long molecules into shorter ones and the sewing of long molecules into cross-linked ones. The first effect is clearly observable by performing the spectrum of the  $\text{CDCl}_3$  soluble fraction of irradiated PB. By comparing

this spectrum with that of nonirradiated PB, a considerable increase of the signal at 4 ppm is observed: see Fig. 4, bottom (nonirradiated PB) and middle (100 kGy). This signal can be safely ascribed to low molecular weight oligomers.

The second effect is only observable by dissolving the  $\text{CDCl}_3$  insoluble fraction of the irradiated polymeric system in a more powerful solvent, such as  $\text{C}_2\text{D}_2\text{Cl}_4$ , and operating





Fig. 8.  $^1\text{H}$  MAS spectra recorded at 200.13 MHz for purified ABS, only the range 7–0 ppm is shown: (bottom) nonirradiated sample; (middle)  $D = 5$  kGy; (Top)  $D = 20$  kGy. A gaussian multiplication function has been applied to improve the resolution enhancement ( $\text{LB} = -64$ ,  $\text{GB} = 0.4$ ).

at high temperature. In the  $\text{CDCl}_3$  insoluble fraction of PB the presence of cross-linked units is pointed out by the appearance of resonances in the 2–3 ppm range, see Fig. 4, top [28,29].

#### 3.4. High-impact polystyrene

High-impact polystyrene is one of the most widely used materials for food packaging. It contains a small amount of poly-butadiene and both BHT and Irganox 1076 as anti-oxidants. For this copolymer the role of additives has

shown to be crucial in preventing damages due to  $\gamma$  irradiation.

No difference can be detected for the stabilized commercial HIPS submitted to irradiation treatment either in  $T_1$  relaxation time measurements or in high-resolution NMR spectra. In turn, differences in  $T_2$  relaxation times are detectable at high doses for purified HIPS, see Fig. 5. Three  $T_2$  components can be measured: a fast  $T_2$  component  $T_{2F} < 0.5$  ms, a slow component  $10 < T_{2s} < 50$  ms and a medium  $T_{2m}$  component. As previously observed, the slow and intermediate components are due to domains of poly-butadiene, while the faster one can be ascribed to the

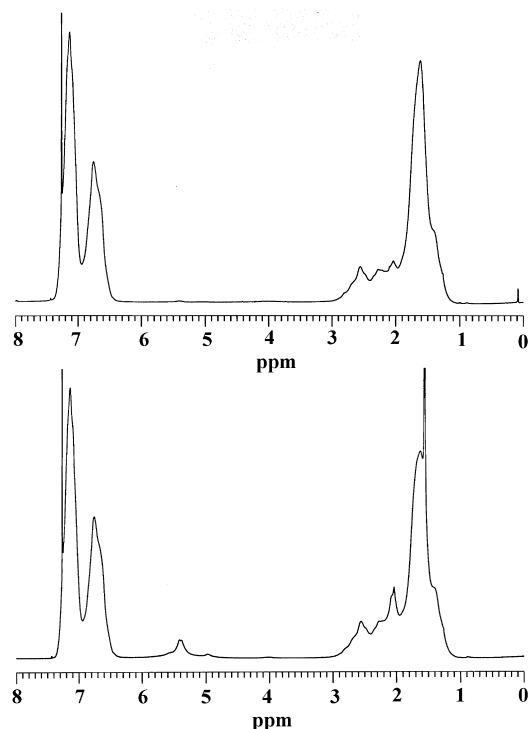


Fig. 9.  $^1\text{H}$  NMR spectra recorded at 600.13 MHz for purified ABS in  $\text{CDCl}_3$ : (bottom) nonirradiated sample,  $T = 100$  K; (top)  $D = 100$  kGy,  $T = 300$  K.

interface PS–PB. The presence of interfaces is also observable using the  $^{13}\text{C}$  MAS technique [19].

This evidence is also confirmed by  $^{13}\text{C}$  MAS spectra of purified HIPS. As a function of the irradiation dose, a progressive decrease of the signals at  $\approx 32$  and  $\approx 28$  ppm due to the mobile PB component of HIPS is observable, see Fig. 6, bottom (nonirradiated sample), top (100 kGy). At high doses ( $\approx 100$  kGy) only resonances from the rigid matrix of polystyrene can be observed, quite unaffected by the irradiation process, while PB gives only poorly resolved broad lines. These results point to a certain level of instability of the purified HIPS upon  $\gamma$  irradiation. In commercial polymers this phenomenon is not observable.

### 3.5. Acrylonitrile butadiene styrene

The ABS copolymer also contains the BHT and Irganox 1076 additives. The presence of such additives in ABS (just as in HIPS) prevents the occurrence of both cross-linking and degradation under  $\gamma$  irradiation. In fact, a considerable amount of radiation induced cross-link occurs in additive-free-HIPS.

In  $^1\text{H}$  MAS spectra, the quite sharp resonances of the PB component of a purified, nonirradiated (0 kGy) ABS sample are easily observable, while the styrene and acrylonitrile rigid components are very broad, see Fig. 7, middle (50 kGy) and top (75 kGy). By increasing the dose of irradiation, a marked, progressive broadening of PB resonances

occurs. At high doses of irradiation a poorly resolved spectrum is obtained, the resonances being due to PB, as broad as the resonances of the stiff styrene and acrylonitrile components, see Fig. 7 (75 kGy).

Progressive broadening is tightly related to the increasing presence of cross-links in the polymeric chain. To show the effect of the irradiation at low doses (0, 5 and 20 kGy), we report the  $^1\text{H}$  spectra relative to peaks resonating in the range 7–0 ppm, see Fig. 8. Even at doses as low as 5 kGy, the loss of spectral resolution is clearly observable.

The effect of irradiation on additive-free HIPS is also well observable when  $^1\text{H}$  NMR spectra of its  $\text{CDCl}_3$  soluble fraction are performed. In Fig. 9 we show the spectra of a nonirradiated sample (bottom), and of a sample submitted to 100 kGy of  $\gamma$  irradiation (top). The resonance at  $\approx 5.5$  ppm is ascribable to PB double bonds. After  $\gamma$  irradiation, the intensity of this resonance decreases, showing a decrease of unsaturated groups. Thus, the presence of cross-links between polymeric chains is univocally demonstrated.

## 4. Conclusions

Knowledge of the chemistry of radiation degradation of polymers is becoming increasingly important on account of the wide variety of applications of polymeric materials [27,30,31].

Irradiation may affect the package directly or indirectly. A direct effect on the physical and chemical properties of polymers results in a general loss of stability, often accompanied by the formation of degradation products [32]. Irradiation may indirectly affect chemical or biological properties, leading to interactions with the packaged product, changing its efficacy or usability [33].

Due to the extremely wide variability of irradiated foods, indirect effects on their packaging have to be established for each particular product and package. In turn, the direct effect of irradiation may be predicted to some extent. Although general guidelines may be drawn, each material must be investigated very carefully for each specific application.

There are two simultaneous effects of irradiation on plastics: degradation and cross-linking, the net result depending on the comparative rates of the two reactions.

According to the literature, polystyrene undergoes cross-linking at high doses of irradiation. Its mechanical properties are also slightly affected only at very high doses. In agreement with these findings, our data confirm that no significant effects can be observed under 100 kGy. Thus, due to its high resistance to radiation treatments, polystyrene is a suitable material for use in the packaging of irradiated foods.

Styrene–acrylonitrile copolymers are not as resistant to radiation as polystyrene itself, but are still fairly stable. As in polystyrene, the aromatic ring structure absorbs a large

part of the radiation energy. Poly-butadiene very easily undergoes both cross-linking and degradation. In fact,  $^1\text{H}$  high-resolution NMR spectra show the presence of  $\gamma$  irradiation-induced effects even when a proper amount of stabilizers is added. Addition of stabilizers is also recommended in poly-butadiene-containing copolymers. In fact, as shown by NMR, in purified HIPS and ABS copolymers, the PB component is badly affected by the  $\gamma$  treatment even below the limit of 10 kGy for safe food irradiation. In turn, the threshold for observable detrimental effects is greatly raised by the presence of proper stabilizers. According to our data, commercial HIPS and ABS do not show detectable effects in the investigated range of  $\gamma$  doses.

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