The Effects of High-Energy Radiation on the Surface Chemistry of Polystyrene: A Mechanistic Study

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SYNOPSIS

Irradiation of polystyrene by 15 Mrad gamma or exposure to a 254 nm ultraviolet (UV) light source leads to surface oxidation of the polymer to depths greater than 10 nm as opposed to ~ 3 nm depth offered by either plasma or corona-discharge treatment. Oxidation increases linearly with UV irradiation time. More carboxyl ($O{=}C{-}O$) acid functionality, which increases with depth, was detected for UV-treated polymer. With 3 Mrad gamma irradiation, only hydroxyl ($C{-}O$) groups were detected by XPS as the surface-oxidized species. ADXPS, GPC, and static SIMS data suggest that chain scission is the dominant degradation mechanism for polystyrene exposed to high gamma and UV radiation, respectively. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polymer surfaces are modified to improve the surface properties such as surface energy and chemistry, while maintaining the bulk properties of the polymer. These properties are usually necessary to improve (a) adhesion, e.g., between fiber/resin interface; (b) biocompatibility; (c) printability; and (d) wettability of surfaces for tissue culture applications. The high-energy processes used for the modification of polymer surfaces include corona-discharge, low-pressure O_2 plasma, and ultraviolet radiation.

The reactions between a polymer surface and corona discharge are believed to proceed by a free-radical mechanism via a peroxide intermediate. Using chemical derivatization in conjunction with XPS, Gerenser et al.[1] identified a key hydroperoxide intermediate in corona-treated polyethylene. The peroxy intermediate can lead to cross-linking and functionalization with or without chain scission in the polymer. It was recently demonstrated by argon-ion ablation of untreated polystyrene that production of a surface-free radical is sufficient for reactions with molecular oxygen to occur; it is not necessary to produce oxygen radicals.[2] The oxidation products from the treatments are alcohols, ethers, hydroper-

oxides, carbonyls, epoxys, carboxylic acids, and esters. In applications such as label adhesion, cell adhesion, chemical coupling, etc., the extent of cross-linking or chain scission due to the treatment may be of equal importance to product performance as are the relative distribution and quantity of oxidized functional groups on the polymer surface. Failure to consider short-chain soluble species resulting perhaps from extensive chain scission could have adverse effects on the adhesion and/or mechanical properties (e.g., hardness, tensile strength, fracture stress) of the surfaces. Therefore, it is important to evaluate the degree of cross-linking and/or chain scission due to the treatment of polymers by the various high-energy processes.

Angle-dependent X-ray photoelectron spectroscopy (ADXPS) is a surface-sensitive technique for nondestructive depth profiles (< 10 nm thickness) of polymers. Therefore, ADXPS should be particularly sensitive to changes in the types, concentration, and depth distribution of the surface functional groups. Static secondary ion mass spectrometry (SIMS) can provide structural or long-range information about surface species; hence, it is complementary to XPS.

In this work, ADXPS, size exclusion chromatography, formally known as gel permeation chromatography (GPC), infrared spectroscopy, and static SIMS were used to study the effect of high energy

(corona-discharge, oxygen plasma, ultraviolet, X-ray radiation, and gamma) treatments on polystyrene.

EXPERIMENTAL

Material Treatments

The surfaces studied were commercial injection-molded polystyrene dishes and roller bottles (except films for IR) containing $\sim$ 0.1% zinc stearate slip agent and no mold-release agents. In the corona process, the article is placed on a conveyor and passed under high voltage (40–80 keV/30 mA) electrodes with 1–2 in. clearance between the electrodes and belt. Gamma treatment (3 and 15 Mrad) was accomplished using a Cobalt-60 source. The roller bottle surfaces were treated with a proprietary plasma process at reduced O_2 pressures.

For the ultraviolet (UV) samples, photolysis at a wavelength of 254 nm (200 W) was achieved by an Oriel Corp. low-pressure mercury arc lamp. There was no filtering to isolate this wavelength. A Sylvania F40 black light generated from a fluorescent lamp was used for 356 nm (40 W) UV photolysis. The sample was placed $\sim$ 3 cm from the barrel of the Hg arc source and as close as possible to the fluorescent lamp during exposure.

X-ray irradiation was accomplished with a Siefert Industrial X-ray instrument operated at 275 keV/ 10 mA for 96 h in air, which provided a dose of 12,672 roentgens (ca. 12.7 Mrad).

X-Ray Photoelectron Spectroscopy

The XPS data were obtained on a PHI Model 5500 XPS/SAM Multitechnique spectrometer. The spectra were collected using a MgKα (1253.6 eV) X-ray source operated at 400 W (15 keV, 27 mA). ADXPS spectra were collected at electron takeoff angles (TOA) with respect to the surface normal of 10, 20, 30, 60, and 90° in the large area lens (small solid angle) mode for better peak definition. Some data were obtained on a Hewlett-Packard Model 5950A spectrometer using a monochromatic AlKα (1486.6 eV) X-ray photon source. This instrument has been described elsewhere.[2] Spectra were referenced to the hydrocarbon carbon 1s level assumed to be 284.6 eV. Curve fitting of data generated on the PHI 5500 instrument was accomplished by superimposing a Gaussian–Lorentzian peak function on the experimental data to get the best fit. The HP

5950A instrument utilizes a pure Gaussian chi-squared minimization curve-fitting routine.

Infrared Spectroscopy

Attenuated total reflectance (ATR) Fourier transform infrared spectra were obtained on a Perkin-Elmer Model 1800 double-beam spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) detector. The polystyrene films were pressed against both faces of the ZnSe crystal and the spectra obtained at 8 cm^{-1} resolution by coadding 400 scans.

Size Exclusion Chromatography

Size exclusion chromatography was carried out on a Perkin-Elmer (PE) GPC unit controlled by a PE 7500 computer. Separation was achieved by injecting 25 μL solution of the sample into Styragel columns (mixed bed: 100A, and 50A; 5 μm packing 7.5 mm $\times$ 30 cm), in THF as the mobile phase and a refractive index RI detector.

Secondary Ion Mass Spectrometry

Static SIMS data were collected on a PHI Model 6300 quadruple-based SIMS instrument using a 4.5 keV Xe^{+} primary ion beam rastered over a 1 mm diameter area. The spectra were collected with a current of 60 picoamps/mm^2 and acquisition time was $<$ 3 min. The above conditions assured operation in the static (total ion dose $< 5 \times 10^{12}$ ions/cm^2) mode. Analysis was performed at a sputtered angle of 30° and charge neutralization was accomplished using the PHI Model 06-110 low-energy electron flood gun. The SIMS work was performed at the Physical Electronics laboratory, Eden Prairie, MN.

RESULTS AND DISCUSSION

XPS

The percent total oxygen determined on the polymer surface after 254 nm high-energy UV irradiation from 5 to 60 min exposure times were found to be in the range of $\sim$10 to 35 atomic %, respectively. This indicates that the surface is significantly oxidized over these exposure times. The high-surface oxygen concentration measured for the UV-treated sample is somewhat surprising in that it exceeds the range of oxygen content (typically 10–20%) observed from other high-energy treatments. The sur-

face oxygen-to-carbon ratio, which reflects the extent of oxidation, was found to increase linearly with UV irradiation time.

There was good correlation between the relative concentration of the $C=O$-containing species (aldehyde or ketone, and acid or ester) determined from the quantification of C1s curve-fitted data and the total oxygen (atomic %) as a function of UV dose.

Under 356 nm low-energy UV radiation, XPS did not detect any oxygen incorporation into the polymer surface after exposure for 2 days. This is in sharp contrast to a previous study by Otocka et al.[3] who reported that the extent and character of photooxidation of polystyrene by 365 and 254 nm UV were similar, based on their transmission and multiple-internal-reflection infrared spectroscopic data. The present results suggest most likely that higher-energy UV is required for oxidation of polystyrene to occur. It is also conceivable, but less likely, that photochemical changes could occur within microns of the surface at 356 nm, especially since polystyrene exhibits an absorption maximum at 260 nm due to the benzene ring. Under these circumstances, it is possible that any oxidized species from 356 nm would not be detected by XPS, which has a shallow sampling depth ($<$ 10 nm). In contrast, infrared with a penetration depth $>$ 0.5 μm, used by Otocka et al. in their study, would be able to detect the photooxidized species. A recent plasma desorption mass spectrometry report by Quinones and Schweikert[4] showed that polystyrene film is photooxidized only at wavelengths $<$ 300 nm UV light. This observation is in good agreement with the results reported in this work. The authors rationalized the inability to detect any changes that may be attributable to photooxidation at wavelengths $>$ 300 nm in the plasma desorption spectra as indicative of the absence of chromophoric groups absorbing at that wavelength in the polymer.

A typical curve fit of the C1s narrow-energy spectrum for the high-energy (corona, UV, and gamma)-treated polystyrene surface is illustrated in Figure 1. The results are consistent with the formation of alcohol, ether, peroxide, or epoxy (286.1 eV), aldehyde or ketone (287.2 eV), and carboxylic acid or ester (288.9 eV).

Both the corona- and gamma-treated surface showed a weak band (291.3 eV) that is due to the polystyrene ring $C=C$ shake-up satellite. The inability to detect this band in the UV- and X-ray-treated samples suggests destruction of the polymer aromatic ring by both treatments. This observation is consistent with an earlier report by Clark and co-workers.[5] With the 3 Mrad gamma-treated surface,
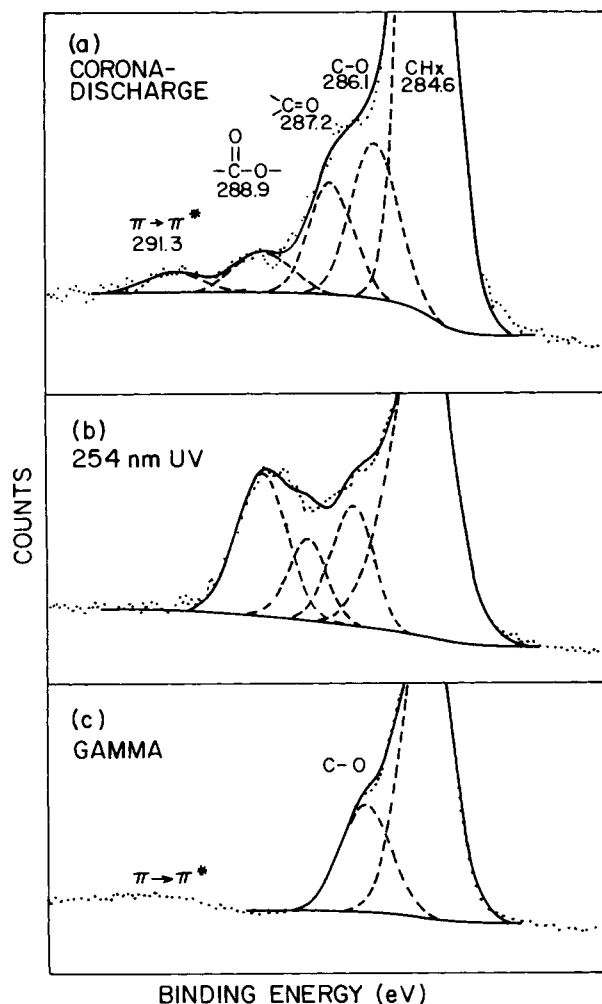
Figure 1   Relative distribution of surface functional groups: (a) corona-discharge-treated; (b) 254 nm UV irradiated; (c) 3 Mrad gamma-treated polystyrene.

the hydroxyl $C=O$ (286.1 eV) was the only functional group detected by XPS. A single broad oxygen peak centered at 532.2 eV was observed in the O1s spectrum of samples irradiated by UV for 5–40 min.

Typically, the O1s spectrum of a carboxyl group shows a peak for carbonyl oxygen at 531.6 eV and a second peak for ester oxygen at 533.1 eV. It appears that the single O1s peak observed at 532.2 eV represents an average energy for a carbonyl and an ester oxygen in a carboxyl group, thus suggesting coalescence of both species in the spectrum. After 60 min irradiation, the O1s spectrum showed two peaks at 532.2 and 535.4 eV binding energies, respectively. The latter peak suggests the formation of singly bound oxygen with a high negative charge such as in carbonates. This assignment was verified from the C1s curve-fitted spectrum that showed an ad-
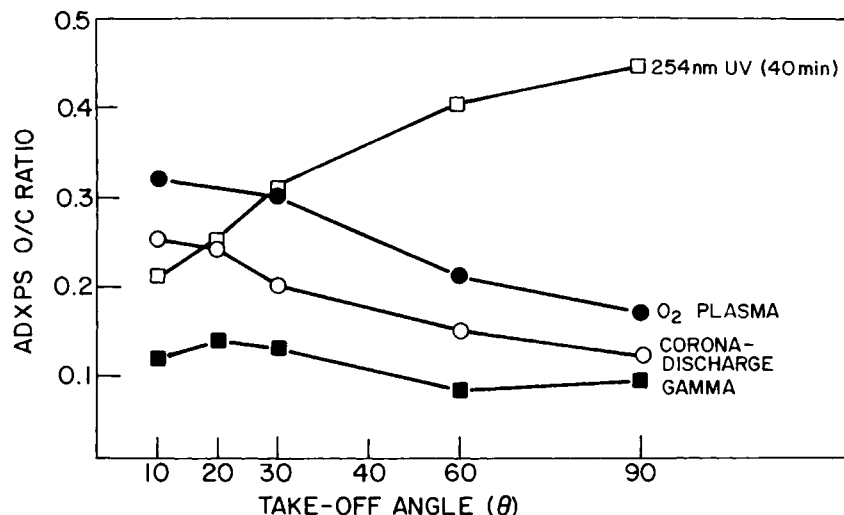
Figure 2 Angle-dependent XPS depth profile showing the depth distribution of an oxidized layer with various surface treatments.

ditional peak at ∼ 290.3 eV, consistent with carbonate formation.[6]

Figure 2 is an ADXPS depth profile spectrum of an O/C ratio as a function of takeoff angle for the various surface treatments. The results show that oxidation is highest at the top surface (10 TOA = 1.5 nm) and decreases as the measurement becomes more bulk-sensitive (90 TOA = 8–10 nm) for plasma- and corona-treated surfaces. This is consistent with a thin oxidized carbon overlayer over bulk polystyrene. Whereas oxidation decreases with depth for corona and plasma, the behavior is quite different for UV and gamma treatments. The gamma profile shows that oxidation is comparatively lower and essentially constant over the sampled depth. The UV profile shows that less photooxidation occurs at the surface and increases substantially into the bulk. This observation is suggestive of either

Table I   Relative Distribution of Surface Functionalities in Polystyrene from Various Treatments as a Function of XPS Takeoff Angle

	Angle (Θ)	Relative Concentration (%)				
		CH_x	C—O	C=O	O=C—O	$\pi \rightarrow \pi^*$
Corona	10	69.8	15.7	7.7	5.0	1.8
	20	68.6	15.9	8.0	5.6	1.9
	30	71.3	15.8	6.2	4.7	2.0
	90	84.6	9.8	2.1	1.5	2.0
Plasma	10	71.1	15.8	6.6	5.3	1.2
	20	69.5	16.4	7.1	5.0	1.9
	30	71.8	14.2	7.3	4.9	1.8
	90	81.5	10.5	2.6	3.4	2.0
UV (254 nm)	10	78.4	10.7	4.1	6.8	—
	20	69.7	17.6	3.6	9.1	—
	30	62.9	17.4	6.9	12.8	—
	90	65.6	14.3	8.0	12.1	—
Gamma	10	88.0	9.0	—	—	3.0
	20	89.5	7.9	—	—	2.5
	30	84.9	10.6	—	—	4.5
	90	84.8	10.4	—	—	4.8
X-ray	45	65.6	19.5	8.8	6.1	—

deeper penetration or excessive degradation by random chain scission of the polystyrene by UV radiation with concurrent oxidation. Table I lists the relative distribution of the carbon-containing surface functionalities of polystyrene subjected to different treatments as a function of reaction depth. The data show that UV photooxidation increases with depth in contrast to either corona or plasma treatment and the increase is most dramatic for $C=O$ and $O=C-O$ groups. For gamma-treated surfaces, the only oxidized species detected are $C-O$ (alcohol, ether, epoxy, or hydroperoxide) groups.

X-Ray Radiation

The X-ray-radiated polymer sample contained $\sim 27\%$ surface oxygen. The total surface oxygen content and the relative distributions of surface functionalities for the sample are identical to those of the UV-treated surface. However, with time, the surface-oxidized species of the X-ray-treated sample was lost completely, presumably in some sort of aging phenomenon, and the spectrum (not shown) was essentially identical to that of untreated polystyrene. Polystyrene modified by other surface-treatment methods loses a small fraction of the surface oxygen species with time but not to the magnitude observed with X-ray radiation.

FTIR

Fourier transform infrared (FTIR) spectroscopy analysis of the UV (20 min)-treated polystyrene film showed a strong carbonyl absorption at 1725 cm^{-1} (spectrum not shown). This band is consistent with either carboxylic acid or the ester group. After soaking the film in methanol for 60 min, the FTIR spectrum showed $\sim 50\%$ reduction in the intensity of this band with no discernible shift in energy. This observation implies the presence of low molecular weight fragments that are soluble in polar solvents. Such species are probably formed by extensive chain

scission due to UV photodegradation followed by oxidation of the fragment species. The solvent removal of the oxidized species in the present work appears to be qualitatively similar to the solubilization phenomenon reported recently by this author for corona-discharge and plasma-treated polystyrene.[7]

GPC

GPC comparisons of the molecular weight distribution of polystyrene subjected to the various treatments are compiled in Table II. The data show similar M_n for UV- and gamma-treated samples that are considerably higher than that of corona-treated and untreated surfaces. The higher number-average (highly sensitive to the presence of small molecules) is consistent with random chain scission process in the polymer under the UV- and gamma-treatment conditions used in this study. The molecular weight distributions (MWD) of the corona-treated sample is identical to that of an untreated surface. This suggests that the formation of low molecular weight (MWT) species is comparatively less under the corona treatment and that the depth of oxidized layer is shallow with corona compared to gamma and UV treatments. Strobel and co-workers[8] showed recently that the amount of low MWT-oxidized material formed on polypropylene surface increases with the input energy to the corona during treatment. According to the authors, the amount of chain scission is sufficiently small at low corona input energies (< 0.05 J/cm^2) so that no low MWT oxidized materials are generated. It appears that the energy range used in the corona treatment of polystyrene in this study is sufficient to form low MWT scission products.

SIMS

The positive ion static SIMS spectra of corona and gamma-treated polystyrene are reproduced in line

Table II   Molecular Weight Distribution Changes of Polystyrene Exposed to Various High-Energy Treatments

Treatment	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
Untreated	17,000	44,300	55,400	2.61
Corona discharge	16,300	44,300	55,400	2.72
Gamma (15 MRad)	31,500	45,000	58,600	1.43
UV (254 nm)	32,600	45,400	56,800	1.39

$\bar{M}_n$, number-average molecular weight; $\bar{M}_w$, weight-average molecular weight; $\bar{M}_z$, z-average molecular weight; $\bar{M}_w/\bar{M}_n$, polydispersity.

form (Fig. 3) for ease of comparison to the untreated "control" sample. For polystyrene, the positive ion spectrum is the most informative, and the most significant chemical changes occur in the 1–100 mass range; hence, only these data are presented. The 15 Mrad gamma spectrum is identical to that of untreated polystyrene and shows the characteristic fragmentation pattern for aromatic hydrocarbons. The assignment of hydrocarbon fragment peaks in this study is in good agreement with the static SIMS studies of saturated and unsaturated aliphatic hydrocarbon polymers reported recently by Briggs.[9] In contrast, the mass spectra of corona-treated poly-

styrene showed a significant reduction in the tropillium ion at 91 amu (atomic mass units) with concomittant enhancement of low (0–60 amu) fragment ions. The 91 amu peak is characteristic of substituted aromatic hydrocarbon species. These observations are indicative of degradation, scission, or bond breaking of the polystyrene side chain.

Peaks indicative of the presence of aliphatic oxygen-containing molecular ions were also observed. The data suggest that oxidation by corona discharge is restricted to the top monolayers of the surface within the SIMS sampling depth ($\sim$ 3 nm). With gamma, the oxidized layer is considerably deeper
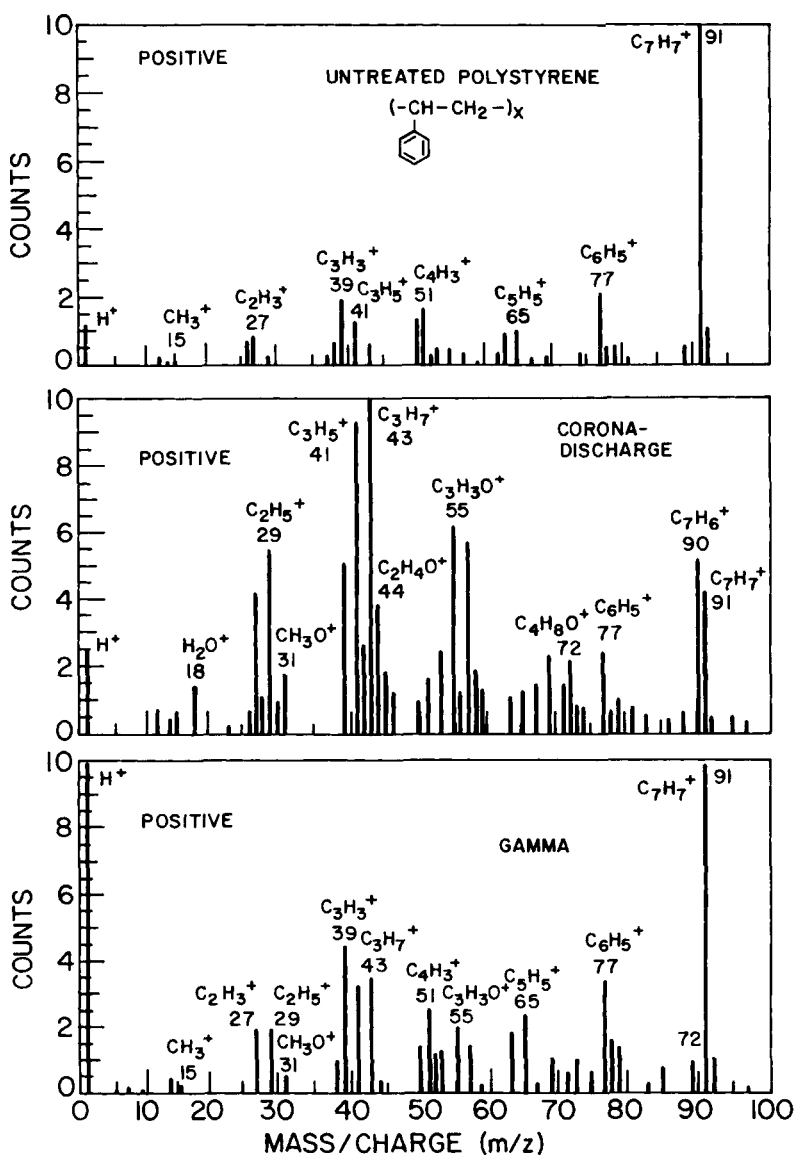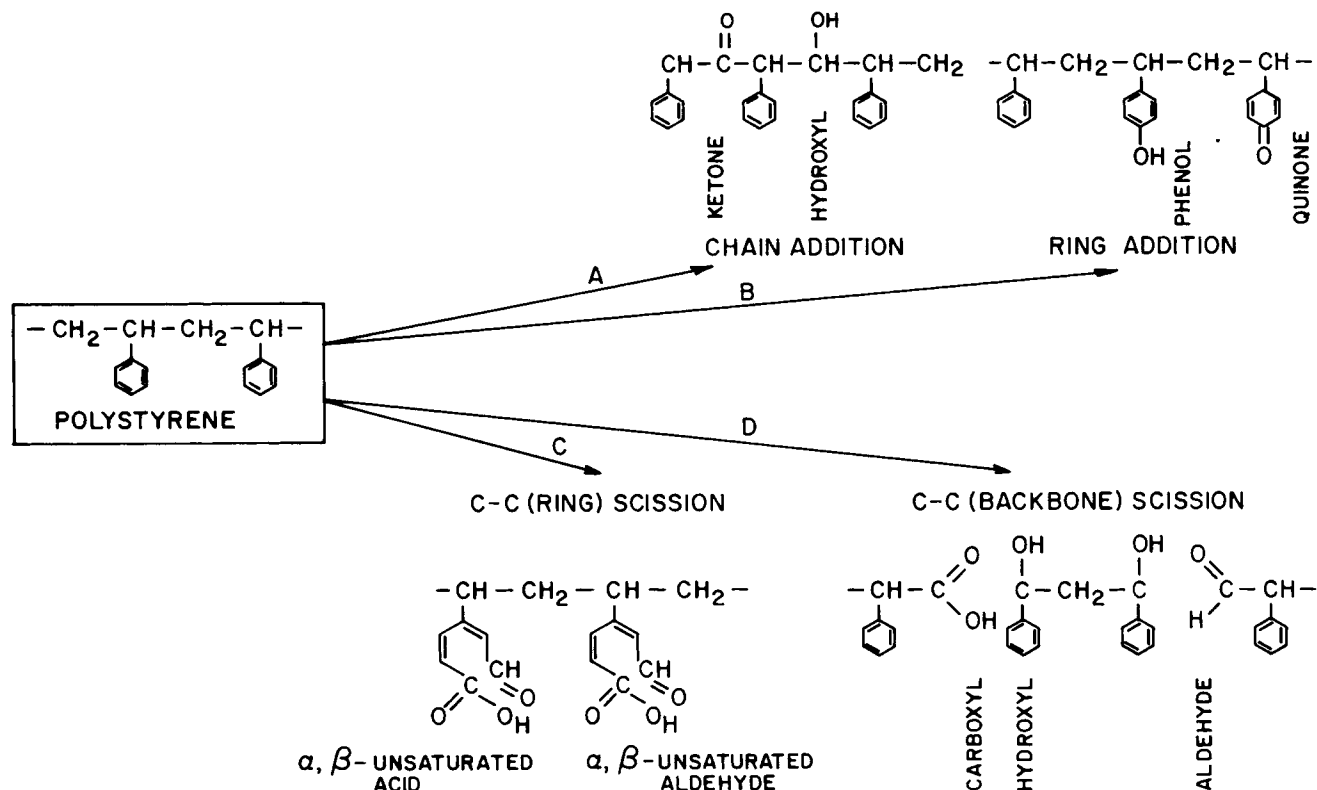

Figure 3 Positive static SIMS spectra of (top to bottom): untreated; corona-discharge; 15 Mrad gamma-treated polystyrene.

Figure 4   Proposed surface oxidation reaction pathways of polystyrene exposed to high-energy treatment.

into the polymer. The corona spectrum also shows the presence of an intense radical fragment ion at mass 90 formed by deprotonation of perhaps an unstable benzyl $C_6H_5(CH_2)^+$ molecular ion. This observation may be suggestive of perhaps a difference in surface chemistry between corona- and gamma-treated polystyrene.

CONCLUSIONS

The results of this work indicate that photodegradation of polystyrene by UV occurs linearly with time and only at 254 nm wavelengths producing carboxyl functionalities as the major products. With gamma radiation, there is no C — C (ring) scission even though oxygen is incorporated into the polymer as hydroxyl groups. UV irradiation and X-ray irradiation lead to opening of the polystyrene aromatic ring and comparatively much higher oxygen incorporation into the surface. Whereas the corona profile decreases linearly with depth, the UV profile exhibits a dramatic increase with depth and the gamma profile shows a relatively flat oxidation level over 1–10 nm sampling depth.

This study offers strong evidence of chain scission as the primary degradation mechanism of polystyrene subjected to high-energy UV and gamma surface treatments. Figure 4 offers possible reaction pathways for surface oxidation of polystyrene exposed to high-energy radiation treatments. Based on the experimental results of this study, it appears that gamma radiation results in the scission of the alkyl side chain C — C backbone (reaction D), whereas with UV irradiation, scission of the phenyl ring C — C (reaction C) appears to dominate. With corona discharge and plasma treatments, surface oxidation can occur via any of the reaction pathways except (C), which involves scission of the C — C bond in the phenyl ring.

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