

Electron Beam Modification of Polyethylene and Polystyrene

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ABSTRACT: Polyethylene (PE) and polystyrene (PS) samples were irradiated in air with 14.89 MeV electrons at the flux of 247 Gy min⁻¹ and the structural changes induced by the irradiation were characterized using UV-vis and IR spectroscopies, differential scanning calorimetry (DSC), and gel permeation chromatography (GPC) and by measuring the contact angle. It was found, in accord with previous studies, that the electron irradiation leads to oxidation of polymers and to splitting of aromatic rings in PS. The surface polarity of degraded polymers increases linearly with increasing electron fluence, the increase being much steeper for PS. No significant changes of crystalline phase or of melting temperature were observed in PE after irradiation. In PS, however, the electron irradiation results in macromolecule splitting and intensive crosslinking. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2529–2533, 1997

INTRODUCTION

Exposition of polymers to ionizing radiation leads to their modification and degradation,^{1–3} which are of interest from a fundamental point of view and for practical applications as well. On the microscopic level, the polymer degradation is characterized by macromolecular chain splitting, creation of low mass fragments, production of free radicals, oxidation, and crosslinking. These degradation processes affect some macroscopic properties of the modified polymers, such as mechanical strength, color, and electrical conductivity. The degree of the degradation and the character of structural changes depends on the type of the irradiation applied, especially on the mechanism

of energy dissipation. From this point of view, energetic electrons are of interest because collisional effects are negligible due to low projectile mass and the energy is dissipated mostly via electronic energy loss. Moreover, with electrons, high deposited energy densities are readily available on modern electron accelerators.

There are several studies of polymer degradation by irradiation with electrons. For example, in Ref. 4, the competition of macromolecular splitting and crosslinking was reported for polyethylene irradiated with 8 MeV electrons. In the same study, the C₃ and C₄ segments as degradation products were detected during the electron irradiation of polypropylene. The irradiation of polyolefines with 12 MeV electrons was reported to result in creation of free radicals and to an increase of free volume fraction as well.⁵

This study was continuation of our previous work^{3,6–9} dealing mostly with polymer modification with heavy ions. The structural and chemical changes induced by irradiation with energetic

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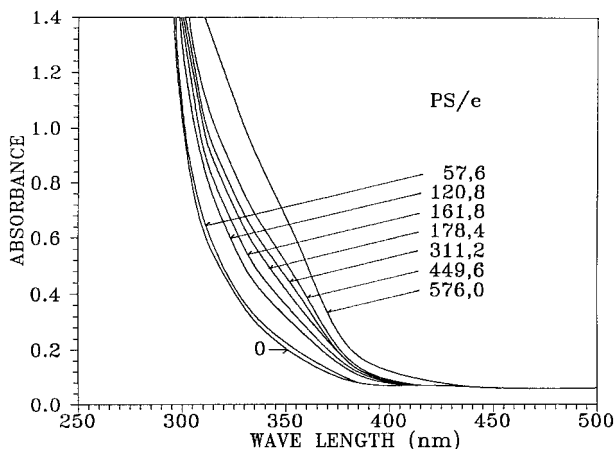


Figure 1 UV-vis spectra of PE irradiated with 14.89 MeV electrons to different fluences. The numbers are the electron fluences in kGy.

electrons in polyethylene and polystyrene were examined using a broad spectrum of diagnostic techniques.

EXPERIMENTAL

The present experiments were accomplished on polyethylene (PE) foils, 15 μm thick ($M_n = 180,000$, $\rho = 0.945 \text{ g cm}^{-3}$) and on polypropylene (PP) sheets, 1 mm thick ($M_n = 100,000$, $\rho = 1.05 \text{ g cm}^{-3}$). The specimens were irradiated in air and at room temperature with a 14.89 MeV Microtron BMT 25 electron beam. The electron flux was 247 Gy min^{-1} and the samples were irradiated to the fluences from 57.6 to 576 kGy.

The UV-vis spectra were measured using a common Perkin-Elmer UV spectrometer. The IR spectrometry was performed using an FTIR spectrometer Nicolet 740. IR and UV spectra were measured twice, 2 and 6 weeks after the ion irradiation, and no significant (i.e., of experimental errors) differences between both spectra were observed. Differential IR spectra are also presented which were obtained as a difference between the IR spectra of irradiated samples and pristine ones. Differential IR spectra measured at constant specimen thickness and with a stable base line make it possible to detect positive or negative changes in the absorption maxima even for very low absolute changes. The polar component of the surface Helmholtz energy, γ_s^p , characterizing polymer surface polarity, was determined by measuring the contact angle with a reflection goniometer (for experimental details, see Ref. 6). Molecular

weight was determined using gel permeation chromatography (GPC) using a Waters 150C device in tetrahydrofuran. The molecular weights were evaluated according to the normalization area, $W(t)$. The GPC column was calibrated for a PS molecular weight up to 2.3×10^6 . The content of the crystalline phase and the melting temperature were determined via differential scanning calorimetry (DSC) on a DuPont 8900 device using a 10 K min^{-1} temperature growth.

RESULTS AND DISCUSSION

It is well known that the irradiation of polymers with ionizing radiation leads to coloration which is attributed to the creation of conjugated double bonds.¹⁰ In UV-vis spectra, the presence of the conjugated double bonds is manifested by the increased absorbance and the shift of the absorption edge toward longer wavelengths.¹⁰ The UV-vis spectra measured on the PE and PS specimens modified by electron irradiation are shown in Figures 1 and 2. It is seen that the irradiation results in a significant absorbance increase in both the PE and PS samples. Similar effects were recently reported for poly(vinyl alcohol) irradiated under similar conditions.¹¹ From the evolution of the UV-vis spectra with increasing electron fluence, it may be concluded that the irradiation leads to production of conjugated double bonds. A more pronounced effect on the PS samples is due to the larger thickness of the PS specimens. Since the range of 15 MeV electrons is about 7 cm in materials with $\rho \approx 1.0 \text{ g cm}^{-3}$,¹² it is clear that the present samples are nearly transparent for the

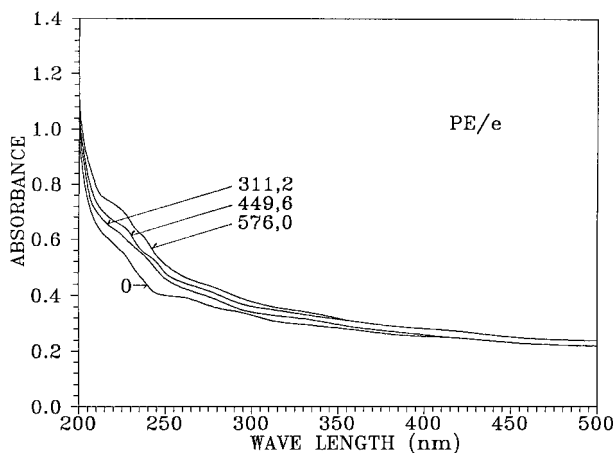


Figure 2 The same as in Figure 1 but for the PS.

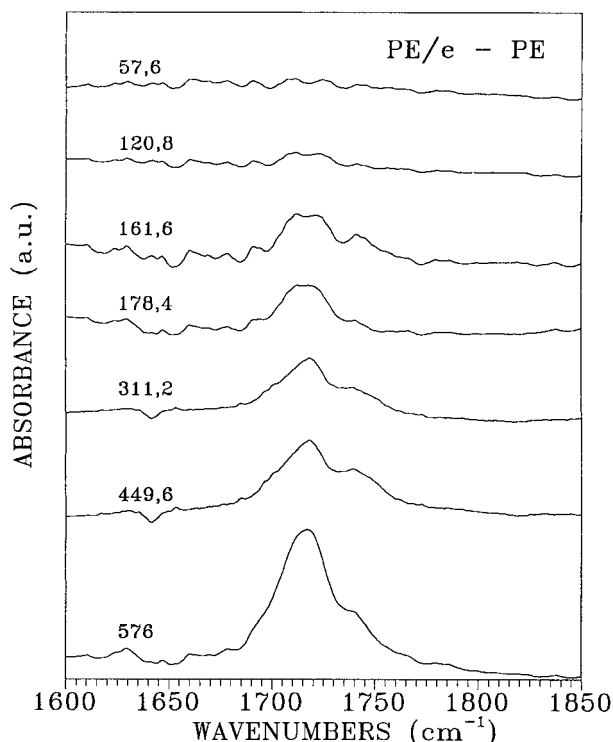


Figure 3 Differential IR spectra of the PE irradiated to different fluences. The spectra were obtained as a difference between the IR spectra of irradiated and pristine PE specimens.

electron beam and only a small portion of the electron energy is deposited within.

The irradiation of polymers in air is accompanied by significant oxidation, which is a result of a diffusion-controlled reaction of ambient oxygen with reactive products of polymer degradation. The oxidation as a function of the electron fluence can be seen from Figure 3 where differential IR spectra, obtained as a difference between the IR spectra from irradiated and pristine PE, are shown. The irradiation to the fluences above 120 kGy leads to a strong increase of the absorbance in the region of 1700–1750 cm^{-1} , attributed to oxidized structures such as carbonyl ($-\text{C}=\text{O}$), carboxyl ($-\text{COOH}$), and ether ($-\text{COO}-$) groups. The concentration of the oxidized structures increases for higher electron fluences but it does not achieve a saturation within the fluence range examined.

Analogous differential IR spectra for the PS specimens are shown in Figure 4. One can see that there is no absorbance increase in the 1700–1750 cm^{-1} region, i.e., the concentration of oxidized structures produced by the irradiation cannot be distinguished under the experimental con-

ditions used. It should be noted, however, that the absorbance was measured in the transmission arrangement, i.e., the whole specimen volume contributes to the measured signal (thickness of the sample of PS is 1 mm). Oxygen can probably penetrate throughout thin PE specimens and produce oxidized structures in the whole sample volume, so that the relative absorbance increase is high and it can easily be detected. On the other hand, in much thicker PS samples, the penetration depth is relatively small and only a relatively thin surface layer is oxidized. So, only a small relative increase of the band $\nu(\text{C}=\text{O})$ vibrations can be expected. Unfortunately, in this region, the $\nu(\text{C}=\text{O})$ vibrations band interferes with overtones and combination bands of the aromatic moiety of PS. As can be seen from Figure 4, the electron irradiation leads to the appearance of an absorption minimum at 1705 cm^{-1} which becomes deeper with increasing irradiation fluence. The 1705 cm^{-1} band is probably of higher harmonics than is the 860 cm^{-1} band, which is attributed to aromatic ring vibration. The present result can be interpreted as an effect of scission of aromatic rings, leading to the creation of fragments enriched with conjugated double bonds which may contribute to the above-discussed changes in UV-vis spectra (see Fig. 1). Even the second minimum at 1735 cm^{-1} (see Fig. 4) is observed for high-fluence irradiation. Also, this observation can be assigned to the decrease of another over-

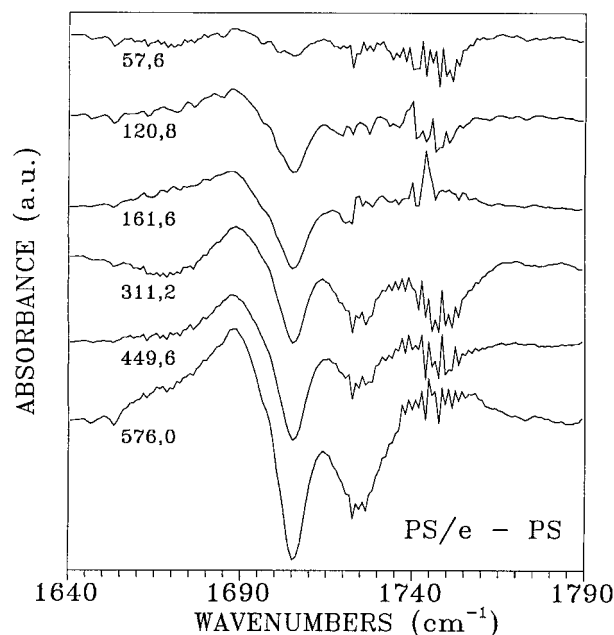


Figure 4 The same as in Figure 3 but for the PS.

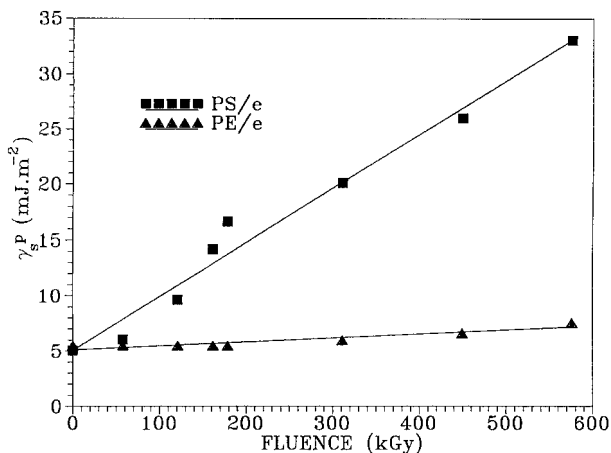


Figure 5 The dependence of the free surface energy, γ_s^p , for PE and PS on the electron fluence.

tone and/or combination band of aromatic moiety. The more remarkable effect of nonoxidizing degradation aromatic rings than the effect of oxidation can be suggested.

The polar component of the surface free energy, γ_s^p , as a function of the irradiation fluence is shown in Figure 5. For both polymers examined, the γ_s^p is a linear, increasing function of the irradiation fluence. Irradiation to the maximum fluence of 570 kGy leads to an increase of γ_s^p by factors of 1.4 and 6.5 (with respect to the pristine polymer) for PE and PS specimens, respectively. This finding is somewhat surprising in view of the known fact that significantly higher fluences are generally needed for the degradation of PS than for PE.¹³ The observed effect may be connected with differences in primary degradation processes as initiated by various kinds of ionizing radiation.¹²

The temperature of melting, T_m , and melting enthalpy, ΔH , of the PE samples irradiated to different fluences were measured using the DSC technique. It was found that, regardless of the irradiation fluence, T_m varies in the interval from 122 to 124°C, and ΔH , in the interval from 150 to 165 J g⁻¹. Since these variations lie within the quoted error, it may be concluded that the irradiation with 15 MeV electrons up to a fluence of 570 kGy does not change the content of the crystalline phase and the melting temperature of the PE investigated. This result is in agreement with a recent X-ray diffraction study of PP modified by irradiation with 12 MeV electrons,¹⁴ where, also, no change in total crystallinity was observed.

It is well known that PE and PS, under irradiation, are vulnerable to crosslinking, which is the

prevailing degradation process at higher irradiation fluences.¹³ Molecular weights— M_w , weight-average, and M_n , number-average, and the polydispersity of PS specimens as a function of the electron fluence are shown in Figure 6. It is seen that up to the fluence of 178 kGy both molecular weights decrease with increasing electron fluence, i.e., the macromolecular chain scission is a dominant degradation process in this region. The scission sites are homogeneously distributed since the polydispersity remains unchanged. In the fluence interval from 178 to 311 kGy, the M_n further decreases, M_w increases, and polydispersity increases very rapidly. These phenomena indicate that in this narrow fluence interval both degradation processes, i.e., the chain scission and the crosslinking, become important. For the fluences above 450 kGy, all relevant quantities, i.e., M_w , M_n , and polydispersity, increase with increasing fluence, so that the crosslinking becomes the dominant structural change. This finding is in accord with some previously published results.¹³

CONCLUSION

The specimens of PE and PS were irradiated with 14.89 MeV electrons in air and the structural changes initiated by the irradiation were studied

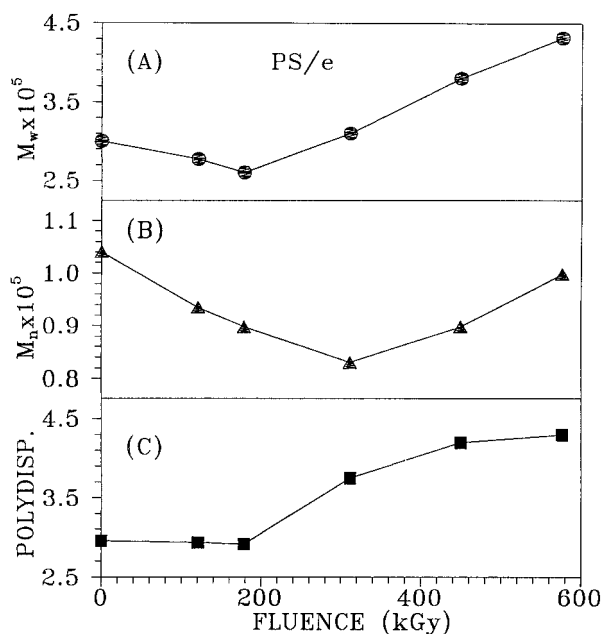


Figure 6 The dependence of molecular weights and polydispersity on the electron fluence. (A) M_w , weight-average; (B) M_n , number-average; (C) polydispersity.

by different techniques yielding complementary analytical information. It was found that the irradiation leads to the production of oxidized structures in PE and to the scission of aromatic rings in PS. The surface polarity is an increasing function of the electron fluence, the polarity increase being much more pronounced in PS. The structural changes in PS are dominated by chain scission for the fluences below 300 kGy and by cross-linking for higher fluences.

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