probable interpretation of decreasing excimer emission with increasing oxygen pressure.

Absorption of incident radiation by pendant aromatic groups will eventually lead not only to excimer formation but also to the dissociation of bonds in a polystyrene backbone. Energy migration may also result in excitation of a small number of chromophoric groups (impurities), which can be expected in commercial samples.

The CTC formation explains why polystyrene can absorb light in the longer wavelength region and can be degraded by light that is not absorbed by molecules themselves. Absorption of light causes dissociation of some bonds into free radicals. In the presence of molecular oxygen peroxy radicals are formed, which readily abstract hydrogen from the same or neighboring macromolecules and form hydroperoxy groups. At that moment secondary reactions play an important role in the observed oxidative scission processes.[15–17]

Acknowledgment. We express our thanks to the Swedish Natural Science Research Council (NFR) for financial support of the project "Study of Contact Complexes between Molecular Oxygen and Polymers under high Pressures".

Registry No. Polystyrene, 9003-53-6; poly(α-methylstyrene), 25014-31-7; poly(p-methylstyrene), 24936-41-2; poly(isopropylstyrene), 30872-09-4; poly(p-chlorostyrene), 24991-47-7; poly(p-bromostyrene), 24936-50-3; O_2, 7782-44-7.

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High-Pressure Photooxidation of Polystyrene

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ABSTRACT: High-pressure (100-bar) photooxidation of polystyrene film has been investigated, and results have been compared with a low-pressure (1-atm) photooxidation. No differences were found between mechanisms of high- and low-pressure photooxidations of polystyrene; however, the kinetics of photooxidation depends on the pressure. Formation of charge-transfer contact (CTC) complexes between molecular oxygen and polystyrene may have an important role in the initiation step of photooxidation.

Introduction

Photooxidation and photodegradation of polystyrene have been widely investigated; however, published papers[1–12] do not give a consistent theory of the photoinitiation mechanism. A major problem is the assignment of absorbing species in polystyrene responsible for light absorption in the region where phenyl groups do not absorb. In extensive photooxidation, new chromophoric groups are formed and may further participate in the absorption of light and in initiation of free-radical oxidation processes. It has been proposed that the initiation of photooxidation in the region of wavelengths greater than 290 nm is due to the absorption of light by chromophoric impurities, e.g., carbonyl groups, and by an energy-transfer process from

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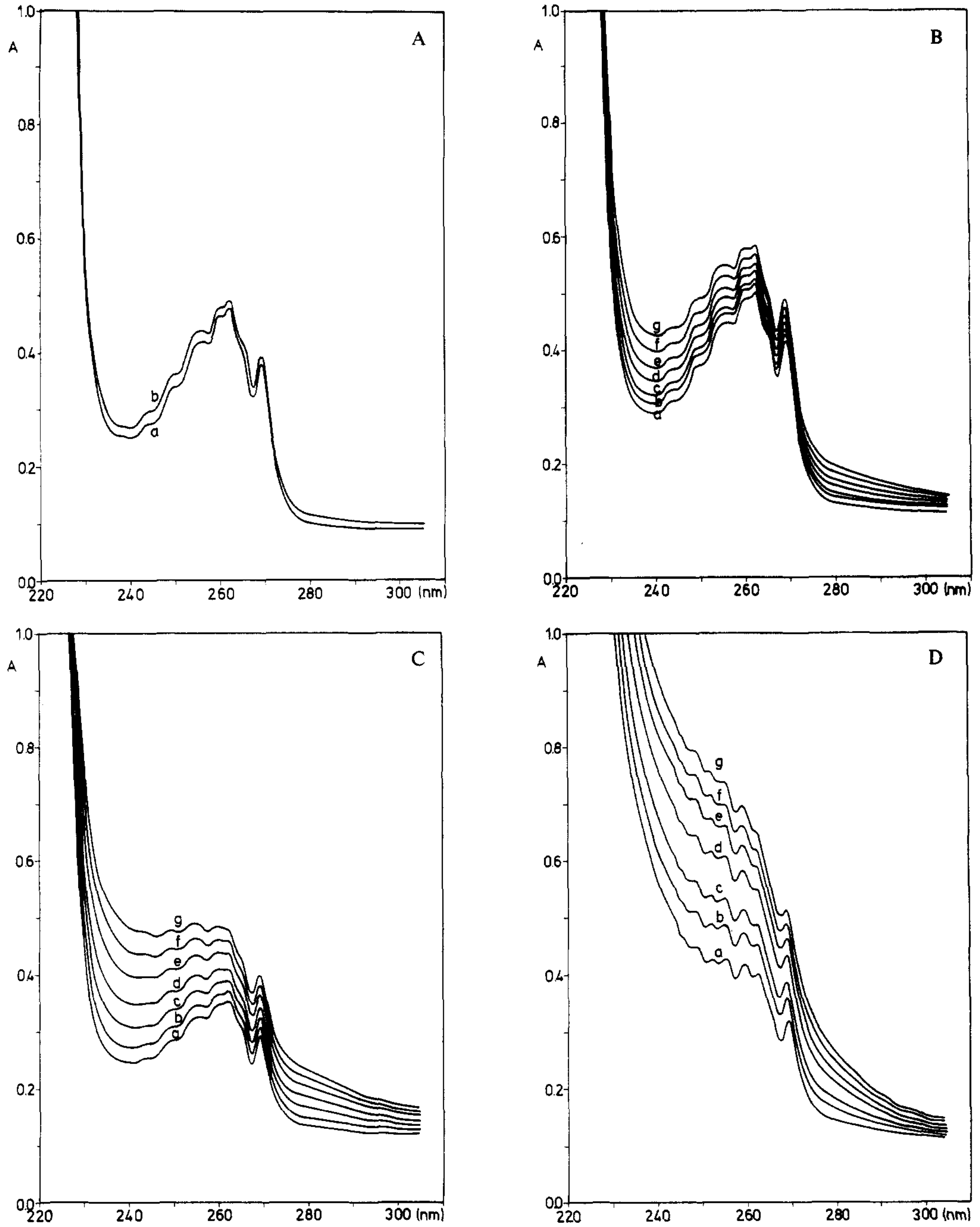

Figure 1. UV/vis absorption spectra of polystyrene films (all 8 μm thick): (A) before (a) and after (b) 1-h UV irradiation (254 nm) under vacuum; (B) before (a) and after 10-min (b), 20-min (c), 30-min (d), 40-min (e), 50-min (f), and 60-min (g) UV irradiation (254 nm) in oxygen under 1-bar pressure; (C) before (a) and after 10-min (b), 20-min (c), 30-min (d), 40-min (e), 50-min (f), and 60-min (g) UV irradiation (254 nm) in oxygen under 10-bar pressure; (D) before (a) and after 10-min (b), 20-min (c), 30-min (d), 40-min (e), 50-min (f), and 60-min (g) UV irradiation (254 nm) in oxygen under 100-bar pressure.

an excited chromophore group to a hydroperoxide group.[13-15] The possibility of oxygen–polymer contact charge transfer (CTC) complexes in extending the light absorption of polystyrene above 300 nm has also been considered.[2,12,16]

In our previous paper[17] we have presented results which show that CTC complexes are formed between polystyrene and molecular oxygen even under atmospheric pressure. Such CTC complexes are very weak, but their absorption increases with increasing oxygen pressure. In this paper we present results on the role of oxygen pressure on the photooxidation reactions of polystyrene.

Experimental Section

Polystyrene (MW 250 000) was supplied by Polyscience, Inc., Warrington, PA. Polymer was additionally purified by dissolving in spectrally pure dichloromethane (ca. 1 wt %) and then precipitated by slowly adding the solution dropwise to stirred methanol under nitrogen. The procedure was repeated four times to ensure that all possible impurities were removed.[18]

The polymer films of 8-μm thickness were placed in an optical pressure cell described elswhere[19] and directly irradiated through a sapphire window (20 mm thick) with 254-nm UV radiation (low-pressure mercury lamp, type HPK 125 W, Phillips, Holland) from a distance of 30 cm under oxygen (medically pure) at different pressures.

Absorption and emission spectra were measured by using Perkin-Elmer 575 UV/vis and LS-5 luminescence spectrometers, respectively. IR spectra were recorded by a computerized Perkin-Elmer 580B infrared spectrometer. The carbonyl index (I_{CO}) and hydroperoxy index (I_{OOH}) were compared to that of the band at 1450 cm^{-1} (a bending mode of $-CH_2-$ in polystyrene).

ESCA core-level spectra for C 1s and O 1s were recorded with a Leybold-Heraus spectrometer by using Al K$\alpha_{1,2}$ excitation radiation. Typical operating conditions for the X-ray gun were 13

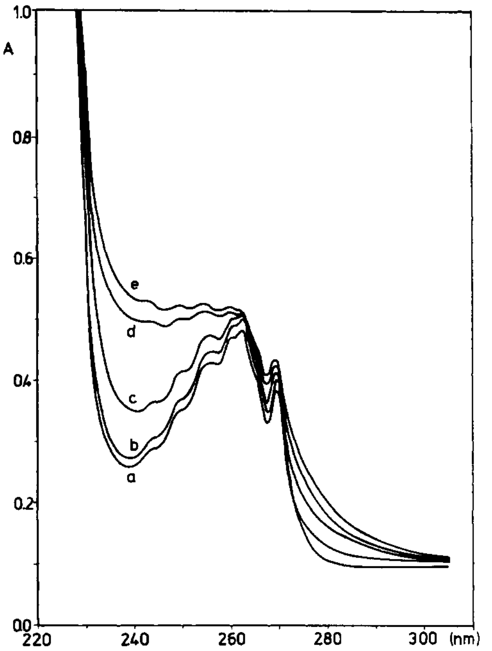

Figure 2. UV/vis absorption spectra of polystyrene films: before (a) and after 1-h UV irradiation (254 nm) in vacuum (b), 1-bar (c), 10-bar (d), and 100-bar (e) oxygen pressure. Measurements were made after reduction of oxygen pressure to 1 bar.

kV and 14 mA and a pressure of 3×10^{-8} mbar in the sample chamber. The electron binding energy in a molecule was calculated from measurements of the kinetic energy of photoemitted electrons by using

$$E_{\mathrm{kin}} = E_{h\nu}(\mathrm{Al\ K}\alpha_{1,2}) - E_{\mathrm{b}} - E_{\mathrm{k}} - W$$

where $E_{h\nu}(\mathrm{Al\ K}\alpha_{1,2}) = 1486.6$ eV, E_{b} is the electron binding energy (eV), E_{k} is the kinetic energy of emitted electrons, and W is the work function (4.6 eV for the instrument used). Line-shape analysis of complex spectral envelopes was made by using a computer curve resolver.

Results and Discussion

The UV/vis absorption spectra of polystyrene film UV irradiated (254 nm) in vacuum (Figure 1A) and at different oxygen pressures (1, 10, and 100 bar) (Figure 1B–D) change continuously with time of irradiation. The final result of photooxidation of polystyrene films at different pressures is shown in Figure 2, where the pressure has been normalized to atmospheric pressure. The difference between UV/vis spectra shown in Figures 1 and 2 is a result of a strong oxygen absorption in the 220–260-nm region, which increases with increasing oxygen pressure, and the formation of contact charge transfer complexes between polystyrene and oxygen under pressure.[17] Absorption spectra shown in Figure 2 show the formation of new absorption in the 270–320- and 230–260-nm regions, which have been attributed to the formation of double bonds along the main chain that are conjugated with phenyl rings.[3,4] These polyene structures are mainly dienes and trienes, but higher polyenes can also be considered. In the 260–280-nm region many other chromophoric groups such as acetophenone, aliphatic ketones, acids, and peracids may also absorb light. Polystyrene film, UV irradiated (254 nm) in vacuum, also shows a change in its UV/vis absorption spectrum (Figure 1A). This change can be attributed to the buildup of conjugated double bond sequences in the polymer backbone. Parts B–D of Figure 1 show that polyenes are formed with a higher yield when polystyrene films are irradiated at higher oxygen pressures. Evidence for the formation of conjugated sequences of double bonds during the photooxidation of polystyrene at atmospheric pressure has also been obtained from fluorescence spectra.[4]

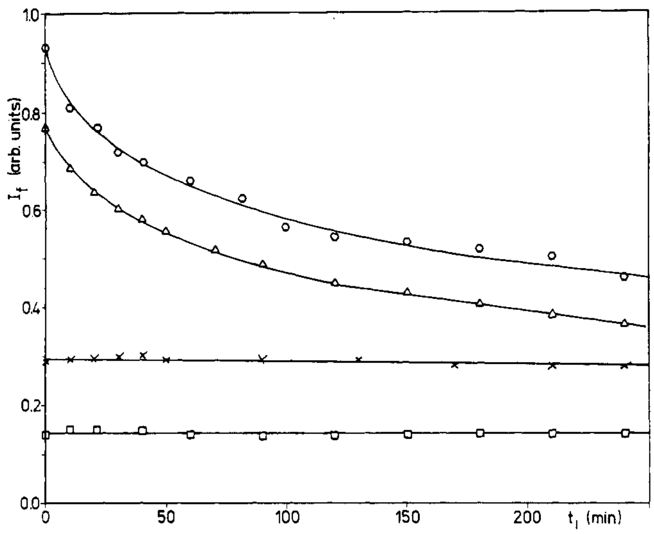

Figure 3. Change in excimer emission of polystyrene films during UV irradiation (254 nm) at different oxygen pressures: (○) under vacuum; (△) 1 bar; (×) 10 bar; (□) 100 bar of oxygen pressure.

Excimer emission of polystyrene film (at 335-nm peak) decreases with increasing oxygen pressure (Figure 3; cf. irradiation time $t_i = 0$), and also during UV irradiation (in vacuum and at 1-bar oxygen pressure) (Figure 3). Excimer emission intensity at higher pressures, i.e., 10 and 100 bar, does not change during UV irradiation (Figure 3). Excimer formation in polystyrene requires close proximity and appropriate relative orientation of the phenyl groups. In the solid state, where the mobility of the polymer chain is considerably reduced, it is therefore assumed that excimer fluorescence is emitted from excimer sites to which absorbed energy can migrate. The decrease in excimer emission during photooxidation of polystyrene can be the result of energy transfer from excited phenyl groups to oxidation products instead of energy migration to excimer sites.[4,8] The absence of change in excimer intensity during photooxidation at 10 and 100 bar (Figure 3) in polystyrene can be explained by a mechanism involving energy migration over short distances to rapidly form excimer sites, which can effectively compete with transfer of energy to oxidation products. During the photooxidation of polystyrene, however, the only detectable new emissions are the fluorescence of polyenes and the phosphorescence of acetophenone groups.[4] Hydroperoxy groups emit neither fluorescence nor phosphorescence.

The IR spectra (Figure 4A,B) show distinctive changes during high-pressure (100-bar) photooxidation (Figure 4B) in comparison to low-pressure (1-bar) photooxidation (Figure 4A). A broad peak at 3100–3600 cm^{-1} appears and can be attributed to the formation of hydroxyl (OH) and/or hydroperoxy (OOH) groups.[4] The kinetics of OH/OOH formation expressed as the hydroperoxy index (I_{OOH}) vs. irradiation time at different oxygen pressures or vs. oxygen pressure changes are presented in parts A and B of Figure 5, respectively. The most dramatic change in peak intensity is observed in the 1730-cm^{-1} band and in the 900–1400-cm^{-1} region (Figure 4B). The carbonyl band at 1730 cm^{-1} has not been firmly established, because of the new interpretation of this band as an aromatic acid group absorption;[10] however, it can be used for monitoring the photooxidation kinetics of polystyrene. The kinetics of this band formation expressed as carbonyl index (I_{CO}) vs. irradiation time at different oxygen pressures or vs. oxygen pressure changes are presented in parts A and B of Figure 6, respectively. In the initial stage of photo-

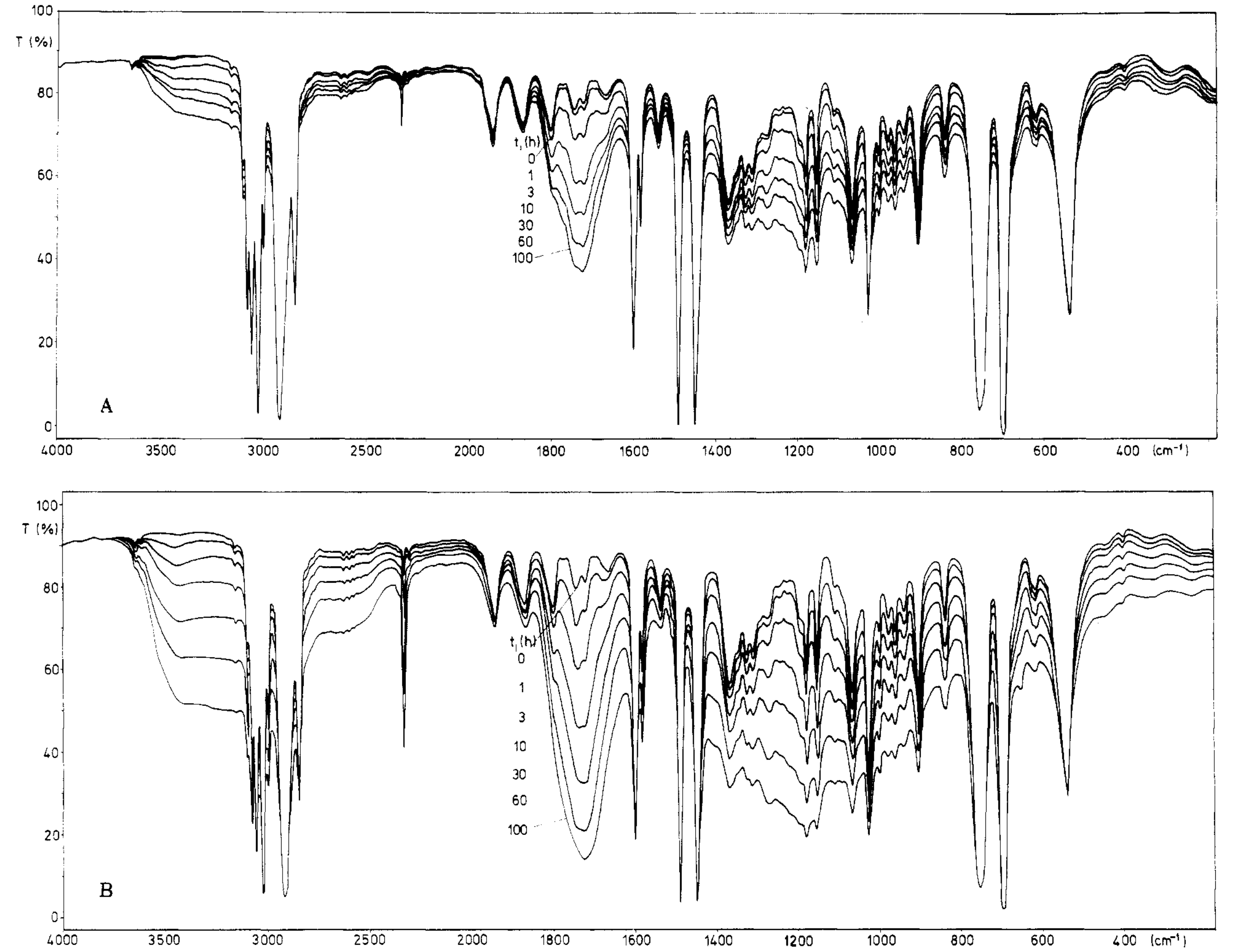

Figure 4. IR absorption spectra of polystyrene films after 1-h UV irradiation (254 nm) at 1-bar (A) and 100-bar (B) oxygen pressure.

oxidation, an acetophenone peak at 1685 cm^{-1}[20] is separable from the 1730-cm^{-1} band (Figure 4A,B); however, after long exposure time this comparatively weak band overlaps the strong 1730-cm^{-1} band (Figure 4A,B). The I_{OOH} (Figure 5B) and I_{CO} (Figure 6B) indices show that the change in rate of OOH and CO group formation is highest at pressures of 1–10 bar and that an increase in oxygen pressure above 10 bar has a very small effect. The I_{OOH} (Figure 5A) and I_{CO} (Figure 6A) indices show that most of the OOH and CO groups are formed during the beginning of irradiation. Rates of formation of OOH and CO groups are not proportional to the increase in oxygen pressure.

It has been spectrally proven that the oxidation rate decreased with increasing penetration depth.[10] This means that photooxidation occurs preferentially at the film surface. ESCA has been employed in our study to follow changes in surface chemistry during high-pressure photooxidation. The relevant C_{1s} and O_{1s} core levels are shown in Figure 7A,B. The C_{1s} derived at 285.0 eV from C–H components in the backbone chain and pendant phenyl groups evidently changes after 100 hours. Computer analysis (Figure 8) shows that the spectrum contains a minimum of three overlapping peaks, which can be attributed to C—O, C=O, and O—C=O functionalities. The intensity of the O_{1s} signal at 534 eV increases during exposure (Figure 7A,B). The nature of oxidized polystyrene surface formed by UV irradiation and a high oxygen pressure is very similar to that observed for exposure in oxygen under atmospheric pressure.[6,7] However, the rate and extent of photooxidation is strongly dependent on the partial pressure of oxygen. With increased pressure oxygen diffuses deeper and is much more soluble in a polymer matrix. The amount of oxygen that is complexed with polystyrene in the form of charge-transfer contact (CTC) complexes increases with pressure.[17] Formation of CTC complexes is not only limited to the surface but may occur throughout the polymer matrix. The diffusion rate of oxygen can be partially reduced by formation of the CTC complexes. The rate of oxygen reaction with photolyzed sites (polymer radicals formed) is no longer limited by the diffusion rate. Excitations trapped at the CTCs are probably ineffective as initiators of photooxidation. The results presented in Figures 5B and 6B show that the rate of oxidation (expressed here as a ratio of intensity of HOO or CO formation per given time of irradiation) decreases with increasing oxygen pressure above 10 bar and then remains constant up to 100 bar. Interpretation of these results is difficult, but one can consider formation of a steady-state condition in which the number of OOH or CO groups formed is almost equivalent to the number of these groups photolyzed.

The mechanism of photooxidative degradation of polystyrene at higher oxygen pressure does not differ from that for photooxidation at atmospheric pressure (Figure 4A,B). It is well-known that polymer alkyl radicals react immediately with oxygen molecules to form polymer peroxy radicals. This reaction should become more efficient as oxygen pressure increases. Polymer peroxy radicals then abstract hydrogen from the same and/or neighboring polymer molecules, and hydroperoxy groups are formed. Further decomposition of these groups produces polymer oxy radicals and hydroxy radicals. The polymer oxy rad-

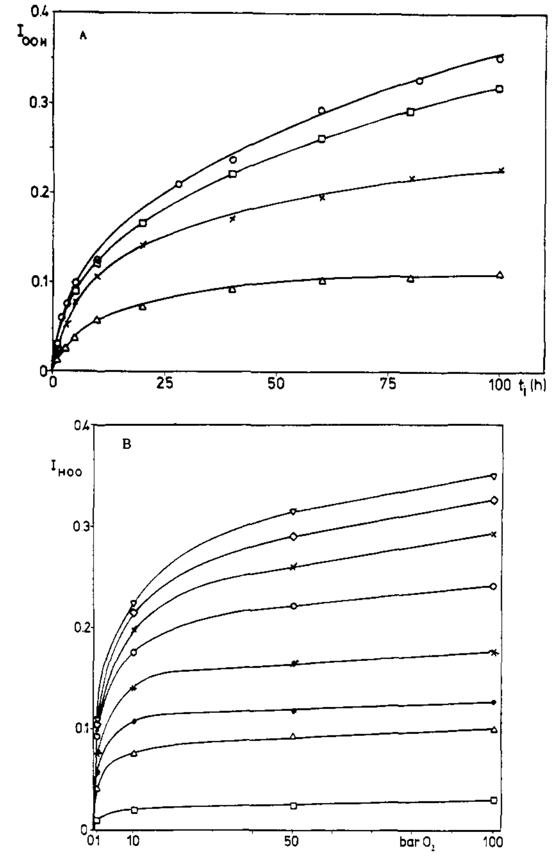

Figure 5. Kinetics of OOH group formation (I_{OOH}) (A) as a function of UV irradiation (254 nm) time (t_i, h) at 1-bar (△), 10-bar (×), 50-bar (□), and 100-bar (○) of oxygen pressure; (B) as a function of oxygen pressure (bar) after UV irradiation (254 nm) for 1 (□), 5 (△), 10 (●), 20 (*), 40 (○), 60 (×), 80 (◇), and 100 (▽) h.

icals are more likely to give aliphatic ketones rather than acetophenone groups because of the cage effect, which makes elimination of a macroradical difficult. The acetophenone groups are formed in the β-cleavage process of polymer oxy radicals.

Hydroperoxide (OOH) groups, acting as energy acceptors from excited phenyl groups, are decomposed efficiently into free radicals, which further initiate secondary oxidation processes.[4]

The charge-transfer (CTC) complexes may play some role in the initiation step of the photooxidation of polystyrene. This complex absorbs light in a longer wavelength range than the polymer itself.[17] Conversely, CTC complexes have no further influence on secondary photooxidation processes of a polymer backbone because a CTC complex is formed only from a phenyl ring and an oxygen molecule.

It has been suggested that the oxygen–hydrocarbon CTC complex is the precursor to thermal autoxidation of hydrocarbons[20] and that absorption in the CTC band leads to photooxidation in a variety of solvent systems. From the measurements of the photooxidation rate dependence on O_2 pressure, substrate concentration, and light intensity for several aliphatic, olefinic, and aromatic hydrocarbons,[21] it has been concluded that a likely initiating step is

$$RH + O_2 \overset{h\nu}{\rightleftarrows} (RH^+ \cdots O_2^-) \qquad (1)$$

Enhancement of singlet–triplet absorption

$$A + O_2 \xrightarrow{h\nu} {}^3A + {}^1O_2 \qquad (2)$$

$${}^3A + O_2 \rightarrow \text{peroxide} \qquad (3)$$

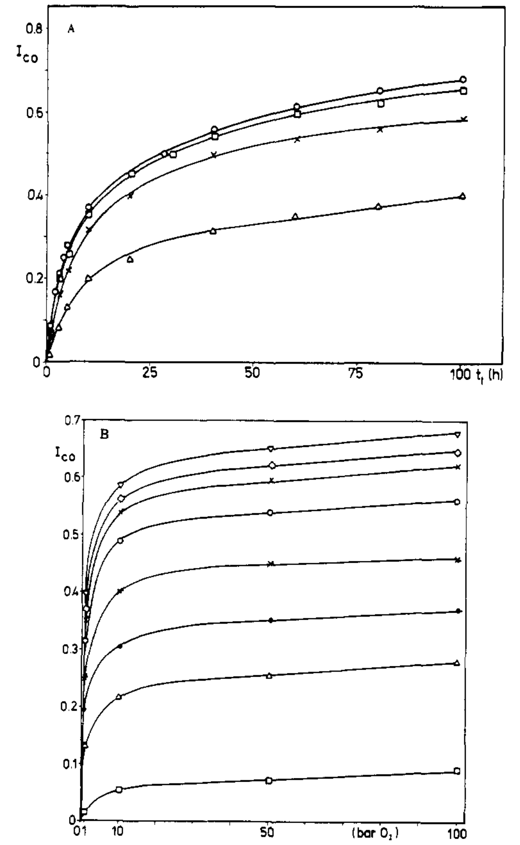

Figure 6. Kinetics of CO group formation (I_{CO}) (A) as a function of UV irradiation (254 nm) time (t_i, h) at 1 bar (△), 10-bar (×), 50 bar (□), and 100-bar (○) oxygen pressure; (B) as a function of oxygen pressure (bar) after UV irradiation (254 nm) for 1 (□), 5 (△), 10 (●), 20 (*), 40 (○), 60 (×), 80 (◇), and 100 (▽) h.

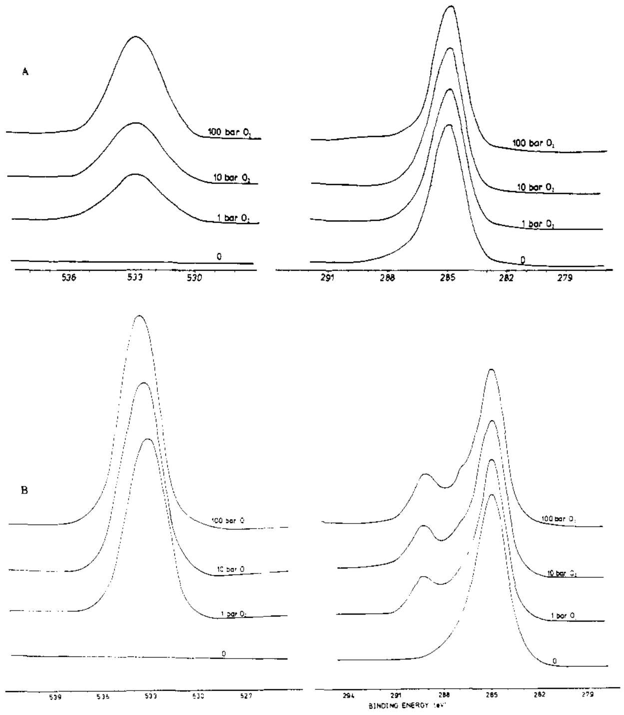

Figure 7. C_{1s} and O_{1s} core levels for polystyrene films UV irradiated (254 nm) in oxygen under different pressures: (A) 1 h; (B) 100 h.

was considered to be important in photooxidation of the olefins and aromatics. However, the same products and product ratios are found in the direct photoexcitation of toluene and in the photoexcitation only within the toluene-O_2 CTC band.[22] These authors concluded that pho-

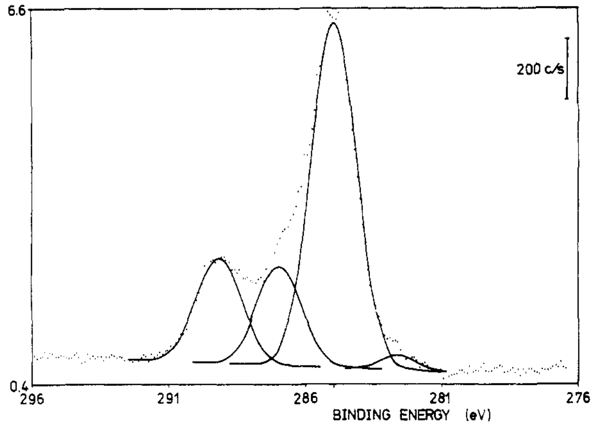

Figure 8. Computer analyzed C_{12} core levels for polystyrene film UV irradiated (100 h) in oxygen at 100 bar.

tooxidation of toluene proceeds via an excited state of the toluene–O_2 contact and not an excited state of toluene or oxygen regardless of the mode of photoexcitation. In addition to reaction 1 another free-radical mechanism involving a second independent photochemical process has been proposed:[23]

$$(RH^{+} \cdots O_2) \rightarrow R\cdot + HO_2\cdot \tag{4}$$

$$R\cdot + HO_2\cdot \rightarrow ROOH \xrightarrow{h\nu} RO\cdot + HO\cdot \tag{5}$$

rather than a concerted insertion of O_2 into the CH bond[24]

$$RH + O_2 \xrightarrow{h\nu} [R + H \cdots O_2]^{*} \rightarrow ROOH \tag{6}$$

Furthermore, by comparing relative rates of photooxidation of cyclohexane and cyclopentane (varying ring size) and relative reactivities of primary, secondary, and tertiary carbons in acyclic hydrocarbons, it was determined that C–H bonds, rather than C–C bonds, are the donor site in the CTC absorption.[24] These results indicate that some differential stability must exist in the charge-transfer precursors, although undoubtedly it is below the operational criterion for contacts.

Our results indicate that the mechanism of polystyrene photooxidation under normal atmospheric or high oxygen pressure is almost the same. However, the rate and extent of photooxidation are strongly dependent on the pressure of oxygen at the gas/solid interface. Although high-pressure photooxidation occurs preferentially at a polymer surface, it also occurs throughout the polymer matrix. This can have an important effect on a number of mechanical, electrical, physical, and chemical properties of a polymer sample.

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Registry No. Polystyrene, 9003-53-6.

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