at the critical composition. Therefore, the phase separation kinetics for PSD/PVME is much faster than that for PSH/PVME with the same degree of superheating simply due to its lower viscosity and higher diffusion constant.

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Registry No. PS, 9003-53-6; PVME, 9003-09-2.

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Charge-Transfer Complexes between Molecular Oxygen and Polystyrenes

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ABSTRACT: Contact charge-transfer complexes (CTC complexes) between polystyrene, poly(α-methylstyrene), poly(p-methylstyrene), poly(p-isopropylstyrene), poly(p-chlorostyrene), poly(p-bromostyrene), and molecular oxygen have been investigated at different oxygen pressures by absorption spectroscopy. At high oxygen pressures formation of CTC complexes increases, whereas intensity of excimer emission decreases. These phenomena are reversible and reproducible. The poly(p-methoxystyrene) does not form a CTC complex with oxygen because of the sterical effect. The main feature of these CTC complexes is the extension of the absorption range of polystyrenes in the presence of oxygen. Formation of CTC complexes may have an important role in the increased absorption of light by polystyrenes and participate in the initiation step of photodegradation.

Introduction

The formation of a charge-transfer complex (CTC complex) between molecular oxygen and organic compounds such as alcohols,[1,2] ethers,[1,3] amines,[2,4] and aromatic hydrocarbons[2,4-6] was reported more than 20 years ago. Styrene forms a CTC oxygen complex, which then participates in the photopolymerization of this monomer.[7,8] The rate of photopolymerization of ethylene is accelerated in the presence of oxygen.[9] This fact has been attributed to the formation of a CTC complex and to an enhanced singlet–triplet transition of ethylene induced by magnetic perturbation due to oxygen.

Formation of CTC complexes has also been proposed for polyolefins[10] and polystyrene.[11-13] More detailed knowledge on the formation of the CTC complexes could

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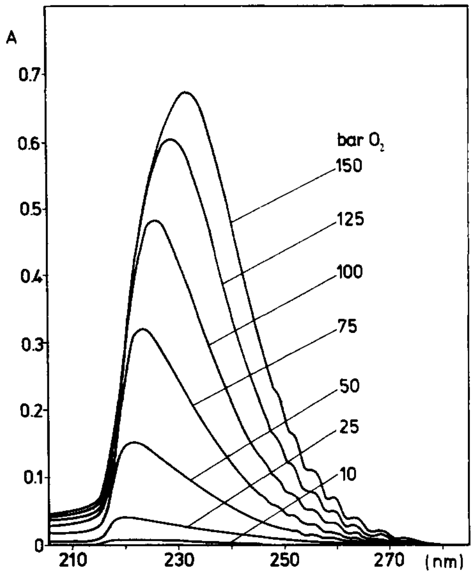

Figure 1. UV absorption spectra of molecular oxygen at different pressures measured as absorbance A) at an optical path length of 1 cm.

be most useful in the interpretation of the photooxidative degradation of polymers and in the design of mechanisms for protection of polymers against photooxidation. Mechanisms of photooxidative degradation of polystyrene have been widely investigated. The published papers, however, do not give a consistent theory, and frequently they are even contradictory.[14-17] A major problem is the interpretation of the photoinitiation step, in which free radicals are formed and further react with molecular oxygen in complex secondary reactions.

In this paper we describe a spectroscopic study of the formation of CTC complexes between molecular oxygen and differently substituted polystyrene under oxygen at high pressure. Polystyrene films were subjected to pressures up to 180 bar, and changes in the absorption and emission characteristics with pressure were observed and recorded.

Experimental Section

Polystyrene (MW 250 000), poly(α-methylstyrene) (MW 960), poly(p-methylstyrene), poly(p-isopropylstyrene), poly(p-chlorostyrene), poly(p-bromostyrene), and poly(p-methoxystyrene) were supplied by Polyscience, Inc., Warrington, PA. The polymer samples were purified by dissolving in spectrally pure dichloromethane (ca. 1 wt %) and precipitated by slowly adding the solution dropwise to stirred spectrally pure methanol under nitrogen. The procedure was repeated four times to ensure extensive removal of possible impurities.[18] The polymer films of 8–10-μm thickness were loaded in the optical pressure cell recently described elswhere[19] and evacuated 24 h by using an Alcacel rotating diffusion pump (France). Absorption and emission spectra (fluorescence) were recorded at pressures of oxygen from 10^{-4} up to 180 bar. The samples were exposed to excitation light in spectrometers for only 2 min for each spectrum taken. This was done to prevent degradation of the samples by photochemical reactions. Absorption and emission spectra were measured by using Perkin-Elmer 575 UV/vis and LS luminescence spectrometers, respectively.

Results and Discussion

Pure oxygen under compression shows an increased absorption band ($^3\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$) (Figure 1), which is a result of the collision of two oxygen molecules.[20,21] The maximum of absorption shifts toward longer wavelengths with increasing oxygen pressure.

High pressures of oxygen have long been known to enhance the $T_1 \leftarrow S_0$ absorption of some organic molecules. The oxygen perturbation effect is particularly strong for aromatic hydrocarbons,[2,5] for which the singlet–triplet absorption is strongly forbidden. The $T_1 \leftarrow S_0$ (π,π^*) absorption is generally enhanced by spin–orbit perturbation. Compounds possessing lowest n, π^* states are not generally sensitive to spin–orbit perturbations, because they already possess a substantial spin–orbit interaction. The enhancement of singlet–triplet absorptions by oxygen observed for organic molecules is a result of interaction between triplet states of these molecules and charge-transfer states.[2,5,22]

The absorption spectrum in polystyrenes orginates from π,π^* transitions and for nonsubstituted benzene ring analogues has considerable fine structure (Figure 2A,B). Substitution of alkyl groups or halogen atoms on the benzene ring produces a disappearance of fine structure and bathochromic shift of the 260-nm absorption band (Figure 2D–G). The absorption for polystyrene (Figure 2A) and for poly(α-methylstyrene) (Figure 2B) increases in the region 230–300 nm with increasing oxygen pressure. In the case of polystyrene these increases in absorption were interpreted as CTC complexes formed between oxygen and polystyrene.[12,13] But this interpretation was partially wrong because the author did not consider the possibility of a strong absorption of compressed oxygen (Figure 1). Pure CTC complexes can only be obtained by subtraction of the oxygen absorption band (Figure 1) from the absorption spectra of examined polystyrene films in the presence of oxygen. The oxygen absorption band does not shift from gas phase to the polymer films when measured through a very thin (0.1–1 μm) polystyrene film on a quartz plate. The corrected CTC spectra for different polystyrenes are shown in Figure 3. These spectra have low absorption (0.01–0.001) because the interaction between molecular oxygen and π-electrons in the phenyl ring of polystyrene is very weak. The CTC absorption band at 275 nm, observed when polystyrene film is exposed to oxygen at high pressure (Figure 3A), is presumably due to a transition from molecular orbitals of the polystyrene aromatic groups. The polarized spectrum for drawn polystyrene-adsorbed O_2 film is stronger for the parallel component than for the perpendicular component, suggesting that the CTC transition moment is perpendicular to the benzene ring.[11] CTC complexes exist even at 1-bar oxygen pressure, but it is particularly difficult to measure these absorption bands. This problem has been overcome experimentally by computer subtraction of spectra shown in Figures 1 and 2A–F. The CTC spectra for polystyrene (Figure 3A) and for poly(α-methylstyrene) (Figure 3B) show an absorption max at 276 nm, whereas substituted benzene ring polystyrenes have their absorption maxima somewhere below 260–280 nm (Figure 3C–F). The CTC maxima for the ring-substitued polystyrenes cannot be measured because of strong oxygen absorption in this region (Figure 1). Poly(p-methoxystyrene) does not form a CTC complex with oxygen even under a pressure of 180 bar (Figure 2G). Employing the computer program *Basic statistics for one- or two-dimensional experimental chemical data* (written by Dr. Z. Hippe, Chemical Center, University of Lund, Sweden), we obtained a simple equation that describes increasing absorption (A) as a function of pressure (P)

$$\ln A = \ln a + b \ln P$$

where a and b are constants which can be related to the diffusion and solubility of oxygen in the polymer matrix. Population of the excited CTC state by absorption of light is thought to occur during collision between oxygen and the benzene ring. The complex has no stability in the

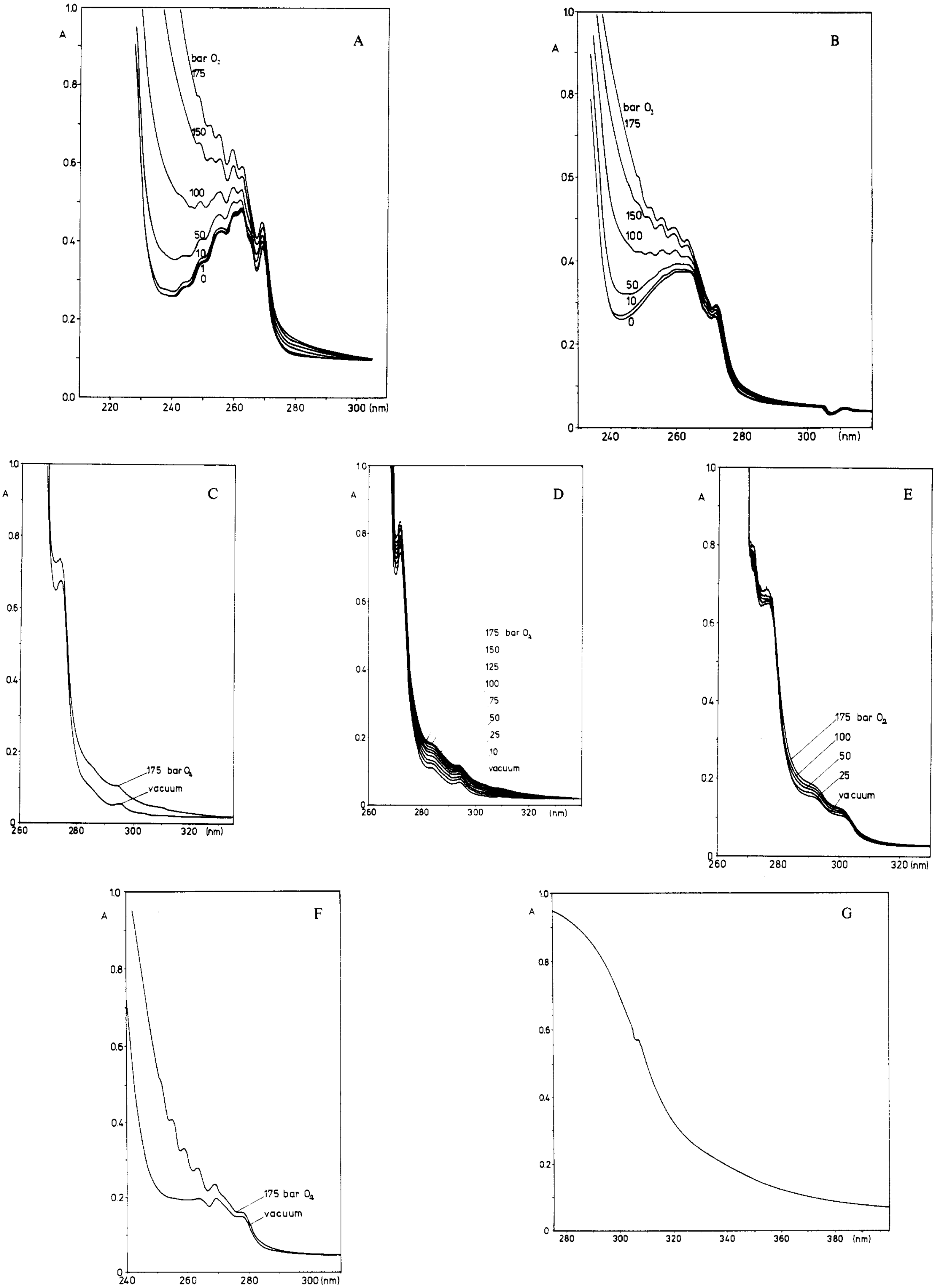

Figure 2. UV/vis absorption spectra of different polystyrene films at different oxygen pressures: (A) polystyrene; (B) poly(α-methylstyrene); (C) poly(p-methylstyrene); (D) poly(isopropylstyrene); (E) poly(p-chlorostyrene); (F) poly(p-bromostyrene); (G) poly(p-methoxystyrene).

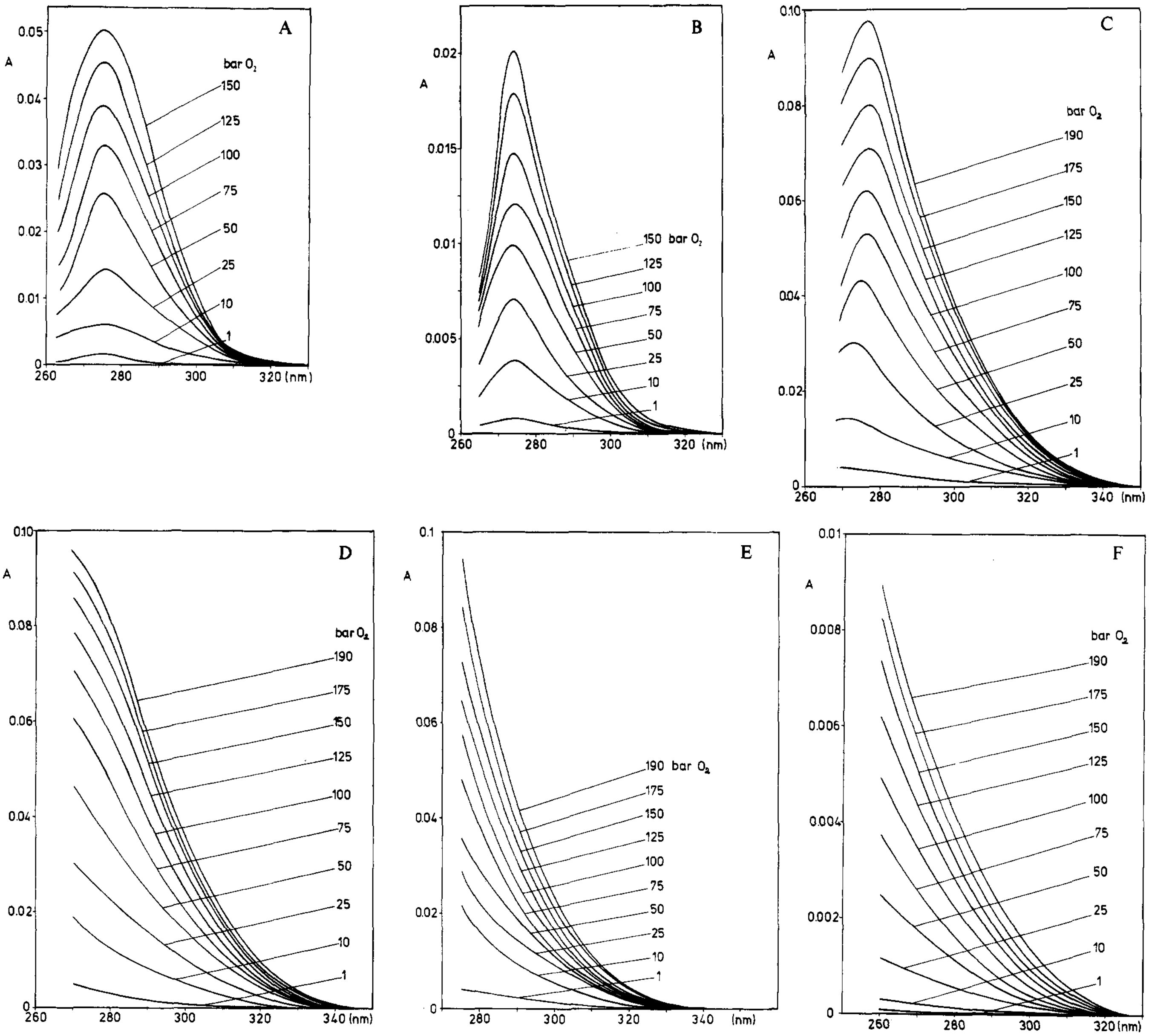

Figure 3. UV/vis absorption spectra of charge-transfer complexes (CTC complexes) between different polystyrenes and molecular oxygen at different pressures: (A) polystyrene; (B) poly(α-methylstyrene); (C) poly(p-methylstyrene); (D) poly(isopropylstyrene); (E) poly(p-chlorostyrene); (F) poly(p-bromostyrene).

ground state; i.e., the equilibrium constant is zero. The main feature of these CTC spectra is the extension to longer wavelength of a polystyrene absorption band on addition of oxygen. The absorption intensity of CTC complexes increases with increasing oxygen pressure that underlies the collisional nature of the interaction. CTC complexes formed from substituted polystyrenes are much weaker than those in polystyrene. Substituted benzene rings are subject to steric perturbations arising from the attached bulky groups, which raise difficulties in an interaction with an oxygen molecule. Such an effect may result in a decrease in the collisional probability for CTC formation. The weaker CTCs could also be interpreted as evidence for changes in the equilibrium constant for the ground-state complexes, which would be expected for hindered rings.

Most substituted polystyrene in the solid state form excimers, which exhibit excimer fluorescence (Figure 4). Poly(p-chlorostyrene), poly(p-bromostyrene), and poly(p-methoxystyrene) do not form excimers that can be observed by fluorescence emission. Absence of excimer fluorescence at room temperature does not imply the absence of excimer formation, because a small enthalpy of formation may lead to rapid dissociation. Polystyrene in solution exhibits two fluorescence bands at 283 and 335 nm, assigned to monomer and excimer emission, respectively,[23-26] Fluorescence from solid polystyrenes have maxima at 335 nm for polystyrene (Figure 4A), 360 nm for poly(α-methylstyrene) (Figure 4B), 314 nm for poly(p-methylstyrene) (Figure 4C), and 312 nm for poly(p-isopropylstyrene) (Figure 4D. In solid polystyrenes a clear-cut distinction between intra- and intermolecular excimers is not easy. Here excimers of a similar symmetry may be formed either within the same polymer chain or between different chains.

The mechanism for excimer formation in solid polystyrenes involves initial excitation of a benzene ring chromophore (π,π^* transition) followed by an energy migration (singlet exciton migration has been considered[37]) along the polymer chain until the excitation is competitively trapped at a chain conformation that is geometrically suitable for excimer formation (excimer-forming sites). Incorporation of energy migration as an excimer site sampling mechanism in polymers is a difficult problem of

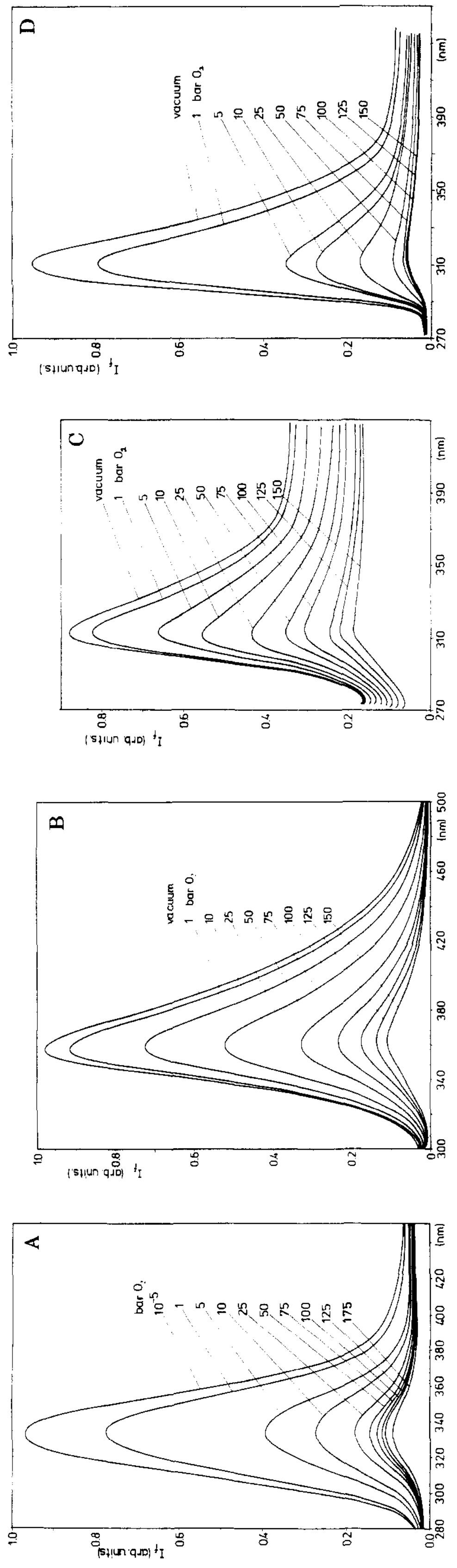

Figure 4. Excimer emission spectra of different polystyrenes at different oxygen pressures: (A) polystyrene (excitation wavelength 260 nm); (B) poly(α-methylstyrene) (excitation wavelength 285 nm); (C) poly(p-methylstyrene) (excitation wavelength 250 nm); (D) poly(p-isopropylstyrene) (excitation wavelength 240 nm).

considerable current interest.[38]

The excimer formation time and the reorientation correlation time for polystyrene (with $\bar{M}_n > 1.0 \times 10^4$) have the same order of magnitude and are about 10^{-5} s.[25-32] This result indicates that the excimer formation of high molecular weight polystyrene is related to local chain relaxations. On the other hand, for polystyrene with $\bar{M}_n < 1.0 \times 10^4$ the rate constant for excimer formation is lower than the reorientational correlation time. This discrepancy is characteristic of intramolecular excimer formation, which is faster at low MW. Excimer formation in polystyrene can be attained more effectively at trapping sites such as crystalline or structural defects rather than by intermolecular interaction. The location of excimer trapping sites in a polymer chain plays an important role in the excimer formation of polystyrene.[33,34]

The excimer of polystyrene cannot dissociate quickly to the excited monomer state since a phenyl group on the polymer chain cannot move as quickly as it can in an aromatic liquid. This restriction of molecular motion accounts for the long residence time for the excimer pair in polymer solid systems, during which they dissipate energy through nonradiative deactivation.

The excimer emission of polystyrenes (Figure 4) is quenched by oxygen as the pressure increases. This phenomenon is reversible and reproducible. Pressures of oxygen up to 180 bar are not sufficient to quench excited singlet states of polystyrenes. Ground-state molecular oxygen ($^3\Sigma_g^-$) is an efficient quencher of the singlet (S_1) and triplet (T_1) states of organic molecules. In general quenching of the S_1 state of aromatic hydrocarbons occurrs at rates close to the diffusion rate.[35] With an oxygen concentration of $[O_2]$ 10^{-2} M at 1 bar and a quenching rate constant of $k_q \sim 10^{10}$ M^{-1} s^{-1}, $k_q[O_2] = 10^8$ s^{-1} at ordinary pressure.[35] Thus excited states with decay rates of the order of 10^8–10^9 s^{-1} will not be efficiently quenched in oxygen-saturated polymers. The situation can change when the pressure of oxygen increases. Both rapid disffusion and greater solubility of oxygen in polymer matrix will then occur. The S_1 state of polystyrene may be more efficiently quenched by oxygen at higher pressures. Increasing oxygen pressure increases the probability of collisional quenching. But, even at 180 bar oxygen pressure, there exist a number of aromatic rings that are not in contact with oxygen molecules and can form excimers. This is one probable interpretation of the decreasing excimer emission with increasing oxygen pressure.

Excimers in polystyrene are formed between two chromophores separated by three carbon atoms along a polymer chain (the $n = 3$ rule of Hirayama).[23] A pair of chromophores that can form an excimer should have a favorable spatial arrangement of a coplanar sandwich type. Strict adherence to such parallel alignment is not necessary. In addition to the geometrical requirements, excimer formation is controlled by the relative motion of the two chromophores. This mobility in the solid state is governed by intrachain flexibility. The stability of an excimer depends strongly on the extent of π-orbital overlap between parallel opposed aromatic rings, but this depends on the energy conformational state.[36] In the aromatic vinyl polymers there are three types of excimer-forming sites: intermolecular; intramolecular, between rings on nonadjacent repeat units; and intramolecular, between adjacent repeat units.

Formation of a CTC between molecular oxygen and a phenyl ring would be expected to hamper the conformational changes required to bring two aromatic rings into a proper position for excimer formation. This is another 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]

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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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