Macromolecules 1993, 26, 3262–3266

Fluorescence Studies of the Vacuum Ultraviolet, Synchrotron Radiation Induced Photochemistry of Polystyrene

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Received June 2, 1992; Revised Manuscript Received November 6, 1992

ABSTRACT: The synchrotron radiation (SR) induced, vacuum ultraviolet (vacuum UV) photodegradation of polystyrene was studied by fluorescence spectroscopy. Two broad, structureless transitions were observed in the dispersed fluorescence spectrum of polystyrene when wavelengths shorter than 2200 Å were used to excite the polymer films: the first was centered at 3200 Å, and the second was centered at 5300 Å. The fluorescence excitation spectrum of each emission band has been recorded from 450 to 3000 Å and is compared to the optical absorption spectrum of polystyrene from 1050 to 3000 Å. The 3200-Å band is due to an excimer to ground state transition. The 5300-Å band is due to fluorescence from a conjugated backbone structure which forms when the polystyrene films are exposed to vacuum UV radiation. Changes were observed in both the fluorescence and fluorescence excitation spectra following exposure to 1200-Å or broad-band SR. Based on the data, a qualitative model is used to account for the degradation and energy transfer within the polystyrene films.

1. Introduction

Polymers are used in the thermal and electrical insulating coatings on satellites and other space vehicles because of their versatility and their light weight; however, when exposed to a space environment for long periods of time (several years), these materials have been shown to undergo severe degradation characterized by discoloration and pitting.[1,2] Much of the degradation is thought to come from the impingement of atomic oxygen which comes from the outer atmosphere. However, even the films on the deep-space side of the satellites, which were shielded from the oxygen, underwent degradation; thus vacuum ultraviolet (vacuum UV) radiation has also been implicated in the degradation of these materials. To develop polymers which are stable to vacuum UV radiation as well as other forms of high-energy radiation, the mechanisms for energy dissipation within polymer films need to be understood.

There have been numerous reports on the photochemistry of polymers induced by wavelengths longer than 2000 Å;[3–8] however, due to the lack of suitable light sources, few studies have been reported at shorter wavelengths. Because synchrotron radiation is tunable from the infrared to the X-ray regions of the electromagnetic spectrum, it is ideal for carrying out polymer degradation studies throughout the vacuum UV region. By exposing polymer films to synchrotron radiation of different energies, the degradation processes which are induced by vacuum UV radiation can be followed systematically.

The purpose of this report is to investigate the role vacuum UV radiation plays in the degradation of polystyrene. Polystyrene, $-(CH(C_6H_5)CH_2)_n-$, was chosen for several reasons. First, polystyrene fluoresces and has been known to give rise to fluorescing degradation products, which would make it possible to follow the photochemistry more readily.[7,8] Second, the lower lying electronic states of polystyrene are closely related to the electronic states of its chromophore, benzene, which has been thoroughly investigated both theoretically and experimentally.[9–14] Finally, there have been numerous photodegradation studies of polystyrene using lower energy ultraviolet light; thus the results of this work can be compared directly to them.

Polystyrene is known to yellow when exposed to UV radiation. Most previous investigators have pointed to the formation of conjugated double bonds along the polystyrene backbone as the reason for the color change. These conjugated sequences or polyene structures not only absorb in the violet region of the visible spectrum but also fluoresce. In vacuum, the chemical reactions that can lead to polyene formation are shown in eq 1 and 2. The first reaction is initiated by the absorption of energy which leads to the dissociation of the α hydrogen from the polymer backbone. The dissociated hydrogen atoms can then abstract hydrogen atoms from neighboring β carbons to form molecular hydrogen and unsaturated bonds in the polymer backbone. The presence of an excited, unsaturated end group can also lead to polyene formation by a hydrogen elimination reaction as shown in eq 2.[5,14]

In this paper we studied the effects of vacuum UV radiation on polystyrene films. Specifically, the absorption, fluorescence excitation and dispersed fluorescence spectra were collected from both free-standing films of polystyrene and thin films spun cast on LiF disks. Because the free-standing films were nontransmitting (~50 μm thick) in the wavelength region studied, they were used to collect the relative cross sections for the fluorescence

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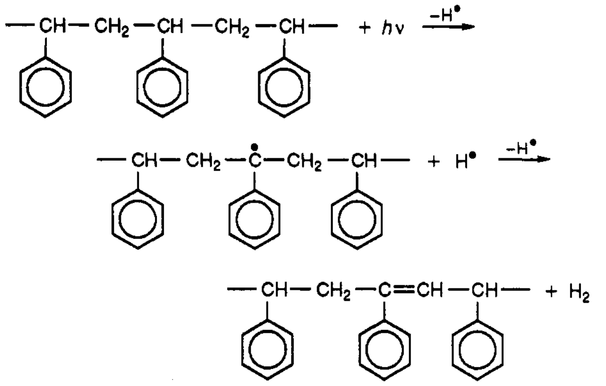

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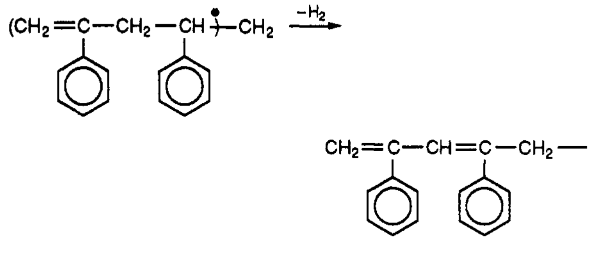

(2)

bands observed in the dispersed fluorescence spectrum. Excitation and dispersed fluorescence spectra were also collected as a function of time of exposure to broad-band SR ($\lambda > 300$ Å) to monitor the chemical changes in the films. The fluorescence excitation and the dispersed fluorescence spectra give direct evidence that degradation products, specifically polyene structures–$(C(C_6H_5)=CH)_n$–, are generated upon vacuum UV exposure.

2. Experimental Section

All measurements were performed on the University of Wisconsin/University of Virginia Seya-Namioka monochromator beamline at the Synchrotron Radiation Center at the University of Wisconsin, Madison. The monochromator employed a 1200 line/mm $AlMgF_2$ grating with a reciprocal linear dispersion of 8.33 Å/mm. Unless specified otherwise, 400-μm slits were used throughout (resolution = 3.33 Å).

Two different chambers were used in these experiments. The first chamber was pumped by a 510 L/s turbomolecular pump resulting in a base pressure of 5×10^{-9} Torr. The second chamber was pumped by a turbomolecular/ion pump system and had a base pressure of 1×10^{-9} Torr. In the first chamber, the sample was oriented so the incident beam was 50° from the surface normal while the fluorescence was collected at 90° from the incident beam. In the second chamber, the sample was positioned so the incident beam was normal to its surface. The fluorescence was collected at a 45° angle from the incident beam. No significant differences were observed in the fluorescence spectra as a result of the two configurations. In both cases an *F*/2 lens collected and collimated the fluorescence after which an *F*/4 lens focused the fluorescence onto the entrance slits of a 0.2-m McPherson vacuum UV monochromator. Slits were normally set to 2 mm, giving a resolution of 160 Å for the fluorescence. A cooled photomultiplier tube and associated electronics were used in the pulse counting mode. Data were collected and stored on a personal computer.

I_0 curves (incident photon flux vs wavelength curves) were collected separately and used to normalize the fluorescence excitation data files. The I_0 curves were measured using a sodium salicylate-coated window/PMT arrangement. Sodium salicylate was used because of its flat response in the energy range studied (450–3000 Å).[15] Using the same sodium salicylate-coated window/PMT arrangement, polystyrene transmission spectra were also collected. Polystyrene absorption spectra were then produced by normalizing the transmission spectra with separately collected I_0 curves.

Both free-standing, thick films (50 μm) and thin films (>0.1 μm) spun cast on a LiF disks were received from the Jet Propulsion Laboratory and used as received. No significant solvent outgassing from the polymer films was seen, and there was no noticeable difference in the spectra collected from samples that were freshly introduced into the vacuum chamber from samples that had been in the vacuum chamber for several hours before being exposed to the excitation beam.

Synchrotron radiation (SR) induced photolysis was performed using both 1200-Å and intense broad-band SR; the latter was achieved by setting the excitation monochromator to "zero order". The relative intensity of the broad-band SR was approximately 1000 times greater than the 1200-Å light.

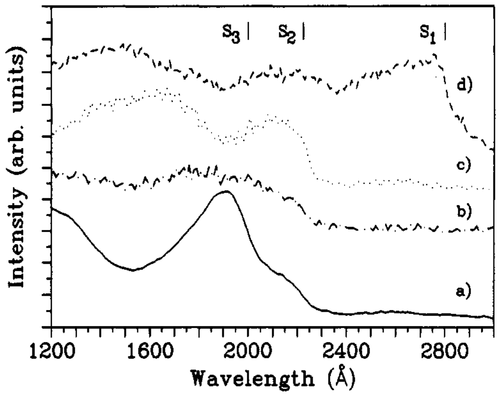

Figure 1. Comparison of the (a) absorption spectrum of a thin polystyrene film to the (b) fluorescence excitation spectra of the 5300- and (c) 3200-Å emission bands that were collected from the same optically thin polystyrene sample after receiving a dose of approximately 1000 mA-min of broad-band SR. (d) Fluorescence excitation spectrum of the 3200-Å emission band from an optically thick polystyrene film. The positions of the S_1, S_2, and S_3 photoabsorption thresholds are marked.[9]

3. Results

3.1. Absorption and Fluorescence Spectra. The absorption spectrum of a thin polystyrene film on a LiF disk, shown in Figure 1a, agrees well with the results reported by both Partridge[9] and Onari.[10] Because the first three excited singlet states (S_1, S_2, and S_3) of polystyrene are well separated in energy, it possible to follow the photophysics and photochemistry of each state separately. The S_1, S_2, and S_3 absorption thresholds in polystyrene are located at 2800, 2225, and 2000 Å and are indicated in Figure 1. These three states correspond directly to the $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ states in gas-phase benzene.[11] Transitions to the S_2 and S_2 states, as well as excitation into the ionization continuum, are clearly seen in Figure 1a. However, since the 2800-Å S_1 transition is forbidden, it is weak and not directly observable in the thin-film absorption spectrum. However, it can be observed in the fluorescence excitation spectrum of the 3200-Å band that was collected from a thick film and which is shown in Figure 1d. Figure 1d will be discussed in further detail below.

The dispersed fluorescence spectrum, which was collected using an excitation wavelength of 1200 Å, is shown in Figure 2. The film had received a dose of approximately 1000 mA-min of broad-band SR. The spectrum consists of two broad structureless transitions centered at 3200 and 5300 Å. The 3200-Å emission is assigned to an excimer to ground state transition in the polymer. Polystyrene has been shown to form excimers both in solution and in the solid phase.[5,16,17] No monomer emission was observed from the polymer films. The 5300-Å emission is assigned to polyene fluorophores which form upon vacuum UV exposure. The reasons for the assignment will be discussed later.

3.2. Fluorescence Excitation Spectra. Spectra b and c of Figure 1 show the thin-film fluorescence excitation

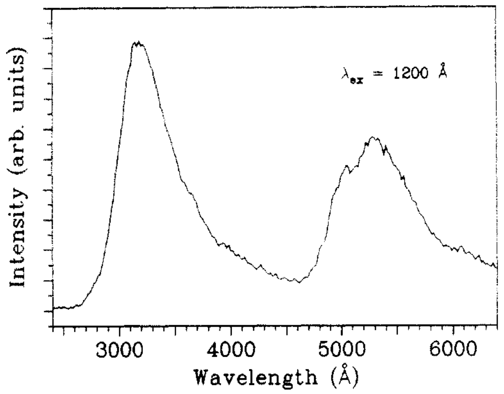

Figure 2. Dispersed fluorescence spectrum collected from the same thin polystyrene film used to collect the spectra shown in Figure 1a–c.

spectra of the 3200- and 5300-Å bands. A comparison of the absorption and the fluorescence excitation spectra clearly shows which of the first three excited singlet states give rise to the two different radiative transitions and that the relative proportions of each are different. First, the excitation spectrum of the 3200-Å excimer band (thick film, Figure 1d) shows that absorption into any of the first three excited singlet states will result in the transfer of the absorbed energy to excimer traps which subsequently fluoresce. The 5300-Å emission results upon absorption into the S_2 and higher lying energy states only.

The thick-film 3200-Å excitation spectrum, shown as Figure 1d, differs from the thin-film spectrum (Figure 1c) because the thick film is fully absorbing; therefore, all transitions are saturated. Thus, spectrum 1d, because it has been normalized to the incident flux, represents the relative quantum yield of the 3200-Å emission band.

Both thin-film excitation spectra exhibit significant departures from the absorption spectrum. In the case of the 3200-Å excitation spectrum, the S_1 and S_2 fluorescence intensities correspond well to the intensities of the S_1 and S_2 absorptions, but the fluorescence intensity which results from the strong S_3 absorption is much weaker than would be expected from comparison with the absorption spectrum alone. Furthermore, the 3200-Å emission band excitation spectrum shows a maximum in the region between 1500 and 1800 Å, whereas the absorption spectrum shows a minimum. Transitions in this region have been assigned mainly to Rydberg and excited σ state transitions, which suggests that these states decay more readily to the S_1 state by internal conversion as compared to the S_2 and S_3 states. The fluorescence excitation spectrum of the 3200-Å band agrees well with the total fluorescence excitation spectra of a solid benzene film as well as benzene in rare gas matrices as reported by Hasnain et al.[18]

The 5300-Å emission band excitation spectrum (Figure 1b) resembles the absorption spectrum more closely, but there are still some very distinct differences—particularly in the relative intensities of the S_3 and S_2 transitions. The ratio of the intensities of the two bands is approximately 2:1 in the absorption spectrum while it is only 1:1 in the excitation spectrum.

3.3. Exposure Dependence of the Fluorescence Spectra. When the polymer films were irradiated with either 1200-Å or broad-band SR, the intensities of the two emissions demonstrated very different behavior. Figure 3 illustrates the behavior of the two transition intensities when a thick polystyrene film was exposed to 1200-Å light. While the 3200-Å band intensity (Figure 3a) remained essentially constant, the 5300-Å band intensity (Figure 3b) tripled.

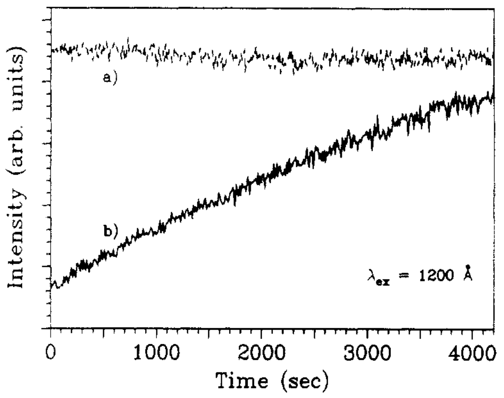

Figure 3. (a) 3200-Å emission and (b) 5300-Å emission intensities as a function of exposure time to 1200-Å light from an optically thick polystyrene film.

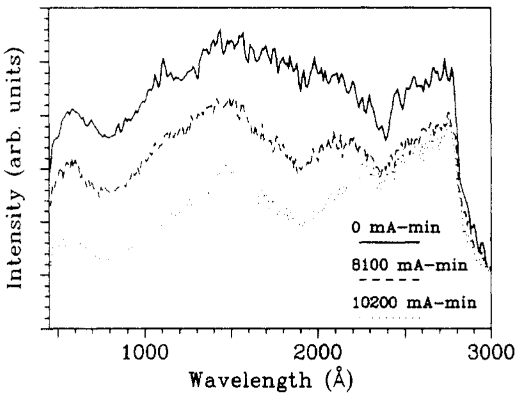

Figure 4. Fluorescence excitation spectrum of the 3200-Å emission band of an optically thick polystyrene film after being exposed to broad-band SR for the amount of time indicated in the figure legend.

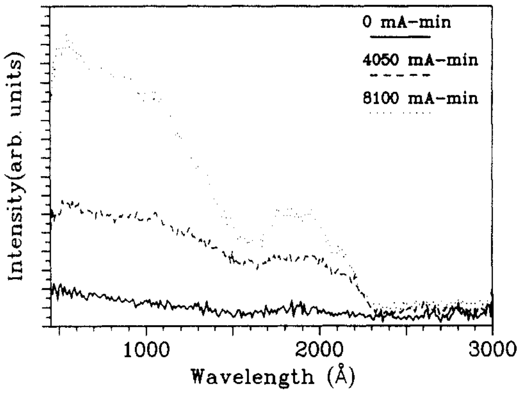

Figure 5. Fluorescence excitation spectrum of the 5300-Å emission band of an optically thick polystyrene film after being exposed to broad-band SR for the amount of time indicated in the figure legend.

Because of the large scattered light background, the signal intensities of the two fluorescence bands could not be monitored when the polymers were exposed to broad-band SR, so a series of spectra were collected at varying intervals of exposure. Figures 4 and 5 show changes in the 3200-Å and 5300-Å fluorescence excitation spectra when thick polystyrene films were exposed to zero-order light. The 3200-Å fluorescence intensity (Figure 4) decreases at all observable excitation wavelengths with increased exposure, whereas the 5300-Å fluorescence excitation spectra exhibited the opposite behavior, with the fluorescence intensity (Figure 5) increasing with increased exposure time.

Finally, Figure 6 illustrates how the dispersed fluorescence spectrum changed when the polymer films were

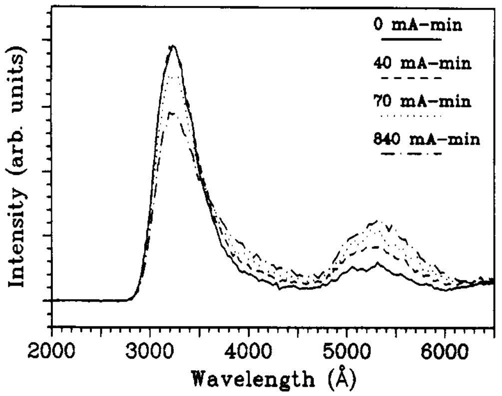

Figure 6. Dispersed fluorescence spectra of a thick polystyrene film after being exposed to broad-band SR for the time indicated in the figure legend (λ_{ex} = 850 Å).

exposed to broad-band SR. Excitation at 850 Å was used for this series of spectra to accentuate the decrease in the excimer band intensity and the increase in the 5300-Å band intensity. As expected from the two previous figures, the 3200-Å emission intensity decreases as the 5300-Å emission intensity increases. The 3200-Å band shown in Figure 6 also broadens upon exposure to broad-band SR.

4. Discussion

The results of the broad-band and monochromatic exposure dependence measurements clearly demonstrate that vacuum UV radiation is effective at initiating photochemical reactions in polystyrene. Previous studies of polystyrene have shown that three basic types of photoreactions can occur: (1) cross-linking, (2) chain scission, and (3) polyene structure formation.[14] Because the products of the cross-linking and chain scision reactions cannot account for the new fluorescence band, we will concentrate on the reactions that generate polyene structure formation. In agreement with our results, previous UV photodegradation studies of polystyrene have also demonstrated that new, longer wavelength fluorescence bands grow with increased radiation exposure.[7,8] The new emission bands are caused by the formation of conjugated, double bonds along the polymer backbone (polyene structures) according to the explanation and chemical reactions given in the Introduction. Grassie and Weir first proposed the mechanism in eq 1 to account for the H_2 that was evolved from UV-irradiated polystyrene films and the changes observed in the UV and IR absorption spectra.[4] The first fluorescence spectroscopic evidence in support of the formation of polyene structures was reported by Geuskens et al.[8] They showed that when polystyrene was irradiated with 253.7-nm light in the presence of oxygen, the excimer intensity decreased with a corresponding increase in fluorescence intensity at 4100, 4600, and 5100 Å. They assigned the new emission bands to polyene structures, $(\mathrm{C(C_6H_5)}{=}\mathrm{CH})_n$, where n was 3, 4, and 5, respectively. They repeated their studies in vacuum and observed emissions consistent with the formation of polyenes ranging in length from 2 to 4 units. They also observed small increases in the UV absorption spectrum at and above 3000 Å in agreement with Grassie and Weir's work.

Lucki et al.[7] carried out photodegradation studies of polystyrene in air-saturated and degassed solutions of cyclohexane, dichloromethane, and chloroform. Unsaturated bonds were clearly formed in both the degassed and air-saturated solutions of polystyrene. The unsaturated backbone structures were observed in the emission spectra with maxima growing in at approximately 3500, 3700, 3900, 4200, and 4500 Å. They also observed significant increases in the absorption intensities of the polystyrene solutions from 2500 to 5000 Å. The longer wavelength absorptions corresponded to the longer wavelength fluorescence bands. The individual peaks were assigned to polyene structures that contained 1, 2, 3, 4, and 5 alternating double bonds.

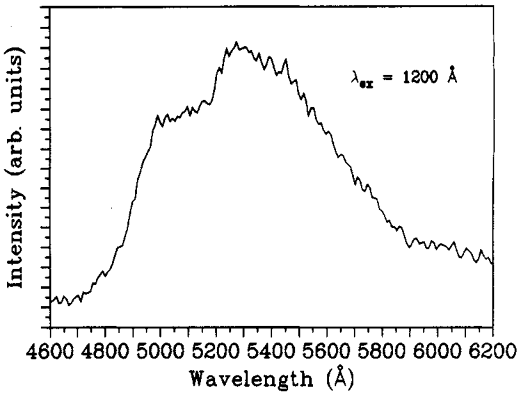

Figure 7. Expanded view of the 5300-Å emission band (λ = 1200 Å; resolution = 80 Å).

Even though the above observations are similar to the observations in this paper, the reported spectra showed multiple fluorescence bands whereas here only the 5300-Å emission band is observed. This apparent discrepancy can be reconciled partly by reviewing the results of Guillet et al., who performed energy transfer studies on styrene–phenylacetylene copolymer (SPA) dissolved in polystyrene films.[19] The SPA fluorescence data offer the best comparison with the present results since the polyene structures are SPA sequences themselves. Because of the method they used to synthesize the SPA films, the average length of the conjugated sequences was 5, e.g.,$-(\mathrm{C(C_6H_5)}{=}\mathrm{CH})_5-$. They demonstrated that energy transfer occurred rapidly (between 4.5 and 7.82 ns) and efficiently from the shorter length conjugated segments to the longer length conjugated segments. When excited with wavelengths from 3800 to 2900 Å, the steady-state fluorescence spectrum of the SPA films showed a very broad fluorescence emission band with its peak located at 4900 Å and a shoulder located at 4200 Å. The shape of the steady-state emission band is similar to the 5300-Å emission band observed in this study. Figure 7 shows a higher resolution (80 Å) spectrum of the 5300-Å emission. It too contains a shoulder at shorter wavelengths (5000 Å).

The strong correlation among the present results, the SPA fluorescence spectra, and the other UV/polystyrene studies indicates that vacuum UV radiation, like lower energy UV radiation, induces polyene structure formation within polystyrene films. However, the 5300-Å emission is longer in wavelength than any of the induced emissions that were observed in previous studies. One possible explanation is that the average length of the conjugated sequences induced by vacuum UV radiation is greater than the average length of the sequences induced by the lower energy UV radiation. The average conjugated sequence length was 5 in the films prepared by Guillet et al., and the steady-state fluorescence band maximum was 4900 Å. Since the chromophore observed in the present study fluoresces at 5300 Å, this suggests that the average conjugation sequence produced by vacuum UV photodegradation is at least 6 units long. Also, the broadening of the 3200-Å emission band and the increase in the fluorescence intensity between the two bands upon increased exposure can be accounted for by the presence of and emission from shorter conjugated sequences.

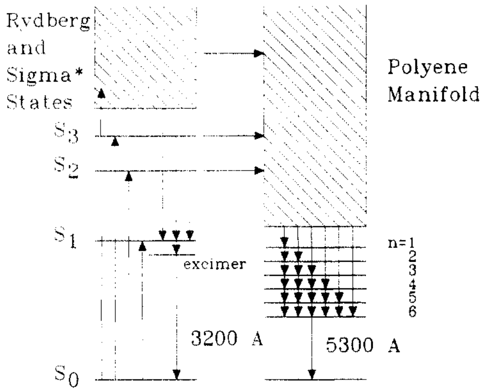

Figure 8. Energy level diagram that qualitatively describes the vacuum UV induced energy transfer of the polystyrene films. The lines labeled $n = 1$–6 represent the lowest lying singlet states associated with the polyene fluorophores which range in length from 1 to 6 monomer units.

With the above assignment of the 5300-Å emission band, a qualitative energy level diagram can be constructed. Figure 8 illustrates the various photophysical events induced by the absorption of vacuum UV radiation. Because the S_1 state does not contribute to the 5300-Å emission signal, we conclude that a negligible amount of energy is transferred from the S_1 state to an existing polyene state when compared to the energy transferred from the S_2 and S_3 states. Excimer trapping may be responsible in part for the lack of energy transfer to polyene fluorophores from the S_1 state. In contrast, the S_2 and higher lying states all contribute to the 5300-Å emission. Therefore, there are channels whereby energy can be transferred from the excited polystyrene states to the polyene states. Because of the large energy difference between the S_2 state and the first excited singlet state of a styrene monomer (represented by the line that is labeled $n = 1$ in the diagram), it is likely that energy is transferred to a higher energy state of styrene or any other longer polyene structures which lies closer in energy to the polystyrene excited state. Once energy has been transferred into the polyene manifold, the energy is transferred rapidly to the longer polyene fluorophores which are directly responsible for the 5300-Å emission. The numbered lines in Figure 8 represent the lowest lying states of the polyene structures which range in length from 1 to 6 monomers units.

The model outlined above also accounts for the static vs the dynamic response of the 3200-Å band intensity that was observed when the polystyrene films were irradiated with monochromatic vs broad-band SR. For example, at an excitation wavelength of 1200 Å, ionization, dissociation, and energy transfer to any photodegradation products (or any other impurities) are all expected to compete with internal conversion as a means for dissipating the absorbed energy. The rate constants for these processes are independent of the photoproduct concentration, but the overall rates are not. Therefore, at high photoproduct concentrations which are generated by broad-band SR exposure, energy transfer rates to the degradation products can become comparable with the rate for internal conversion and draw intensity away from the excimer emission band. At lower photoproduct concentrations (generated during monochromatic light exposures), energy transfer will still occur but will be low enough that no appreciable change in excimer emission band intensity will be seen even though changes in the photoproduct emission band are observed.

5. Conclusions

The results of the vacuum UV photodegradation studies have led to the following conclusions:

1. All wavelengths from 2200 to 450 Å will induce polyene formation in polystyrene films that are irradiated in vacuum.
2. The polyene structure formation can be characterized by a new fluorescence band at 5300 Å in the dispersed fluorescence spectrum when excitation wavelengths shorter than 2200 Å are used.
3. The average number of double bonds in the vacuum UV induced polyene structures is at least 6 compared to 5 or less for UV induced polyene structures.

We have also, to the best of our knowledge, reported the first monochromatic fluorescence excitation spectra of the polystyrene excimer fluorescence band from 3000 down to 450 Å.

Acknowledgments. We would like to thank Dr. Al Stiegman, Dr. Ranty Liang, and Ms. Shirley Chung from the Jet Propulsion Laboratory for useful discussions as well as for providing us with polystyrene samples. We would also like to acknowledge the many contributions made by the SRC staff. Experiments were performed at and partially funded by the Synchrotron Radiation Center, which is supported by the National Science Foundation under Grant DMR 8821625. This research was also partially funded by the Jet Propulsion Laboratory under Contract 958858. We also thank the Olin Corp. for early suppor of this work.

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