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The influence of molecular oxygen and the slip agent, erucamide, on the selectivity of attachment of pyrene to polyethylene chains by >300 nm radiation

Gerald O. Brown, Oscar E. Zimerman[1], Richard G. Weiss*

Department of Chemistry, Georgetown University, Washington, DC 20057-1227, USA

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Abstract

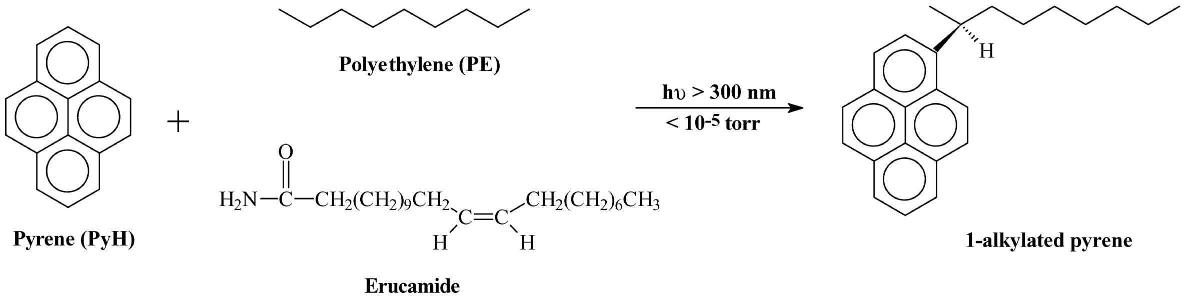
The influence of molecular oxygen and a common slip agent, erucamide, on the selectivity of pyrene attachment to polyethylene chains has been investigated. Films with covalently attached pyrenyl groups are useful to follow microscopic changes that occur when the bulk material is perturbed. Selectivity increases when pyrene-doped low-density polyethylene (PE37) films are thoroughly degassed ($<10^{-5}$ Torr) prior to irradiation. Surprisingly, an increase in selectivity also increases with erucamide content in pyrene-doped PE37 films. Films were characterized using UV/Vis spectroscopy, steady-state and time-resolved fluorescence techniques, differential scanning calorimetry, and X-ray diffraction. © 2002 Published by Elsevier Science Ltd.

Keywords: Erucamide; Polyethylene; Molecular oxygen

1. Introduction

Previously, we have developed techniques for the photochemical attachment of the fluorescent probe, pyrene (PyH), to chains of various types of polyethylene (PE) films [1]. The modified films have been employed to investigate how microenvironments afforded by the polymer chains influence properties of the pyrenyl excited states and to sense how external perturbations affect the micromorphology of the polymers [2]. Our prior attachment method, involving >300 nm radiation in a nitrogen atmosphere [1] produced minor amounts of a second attached lumophore whose structure and origin are unknown. Determination of the factors affecting the selectivity of lumophore attachment is key to our understanding of photophysical processes in polymers and to our interpretations of the influence of various perturbations on the luminescence of modified films.

In this study, we demonstrate that the selectivity of the attachment process can be enhanced by performing irradiations under conditions where traces of molecular oxygen have been removed (i.e. by degassing at $<10^{-5}$ Torr) and by adding various quantities of erucamide [3,4], a common additive in polyolefinic materials that reduces surface friction and enhances plasticity [5].



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* Corresponding author. Tel.: +1-202-687-6013; fax: +1-202-687-6209. *E-mail address:* weissr@georgetown.edu (R.G. Weiss).

[1] Present address: Edge BioSystems, 19208 Orbit Drive, Gaithersburg, MD 20879, USA.

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Table 1
Some properties of polyethylene films

Symbol	Thickness (μm)	Density (g/cm^3)	% Crystallinity[a]
PE32	32[36]	0.900[36]	32 (12)[36]
PE42	38[36]	0.918[10]	42 (24)[36]
PE45	25	0.917	45 (21)
PE76	13	0.952	76 (42)
PE37	263	0.923	37 (26)
PE37-5	298	–	32 (26)
PE37-10	260	–	27 (20)

[a] By X-ray diffraction. Values in parentheses by DSC analyses.

2. Experimental section

2.1. Materials

Before their use, polyethylene films[2] from the Exxon Chemical Company (Baytown Polymers Center, Polyethylene Technology Division, Baytown, Texas), PE45 (LL-3001.63), PE76 (HD7745.10), and PE32 (EXACT 3132) were immersed in several aliquots of chloroform for more than one week to remove anti-oxidants and plasticizers. PE37[2] (Aldrich, Catalogue No. 42,805-1) and erucamide from Aldrich (>87% erucamide content, >97% total amide content) were used as received. Some properties of the films used are summarized in Table 1.

Pyrene (Aldrich, 99%) was recrystallized from benzene, passed through an alumina column using benzene as eluant, and recrystallized twice from ethanol to yield pale yellow crystals, mp 148.6–149.1 °C (lit. mp 149–150 °C) [6]. 1-Ethylpyrene, mp 95–96 °C (lit. mp 94–95 °C) [7] was obtained from Molecular Probes and used as received. Methanol (EM Science, HPLC grade) and chloroform (Fisher, HPLC grade) were used as received.

2.2. Preparation of PE37 films blended with erucamide

Weighed amounts of erucamide and PE37 pellets were heated to approximately 145 °C in a flask while being stirred with a glass rod. When the polymer melted (i.e. became translucent in appearance), the flask was placed in cold water. The rehardened polymer was heated in a press for 1 min at 150 °C under a pressure of 40 kN over a 14 × 17 cm^2 area. PE37 films consisting of 0 wt% (PE37-0), 5 wt% (PE37-5) and 10 wt% (PE37-10) erucamide were prepared in this manner.

2.3. Pyrene-doped PE films

PE films were immersed in solutions of 0.2 M pyrene in chloroform for 1 day, dried under a stream of nitrogen, and their surfaces were washed with methanol (a non-swelling solvent [8]) and dried under a stream of nitrogen. Concentrations of pyrene within the films were determined from the average optical densities of three different spots (Perkin–Elmer Lambda-6 UV/Vis spectrophotometer) and Beers law using the molar extinction coefficient of pyrene in petroleum ether at 335 nm, 55,000 M^{-1} cm^{-1} [9]. They are precise to within ±10%.

2.4. UV irradiation of pyrene-doped PE films

Pyrene-doped PE films in pyrex tubes that were either degassed under vacuum ($<10^{-5}$ Torr) and flame-sealed, purged under a stream of nitrogen for >30 min, or flame sealed under 1 atm pressure of air at room temperature were irradiated (>300 nm) for 1 h at ~10 cm from a 450-W Hanovia medium-pressure Hg arc. Immediately thereafter, the films were soaked in several aliquots of chloroform until UV absorption and fluorescence spectra of the last chloroform wash showed no pyrene or other aromatic species. Finally, they were then dried under a stream of nitrogen. Unless indicated otherwise, all reported spectroscopic data were acquired after this extraction process to remove non-covalently attached lumophores.

Compounds extracted into chloroform from films after irradiation were separated on a Hewlett Packard Series 1100 ChemStation equipped with a diode array detector (4 nm bandwidth) using a Polymer Laboratories PLgel (5 μm; 50 Å; 300 mm length × 7.5 mm ID) size exclusion column and tetrahydrofuran (THF; Fisher Scientific, HPLC grade) as the eluant. Solvent from separated aliquots was evaporated under a stream of nitrogen and hexane (400 μl) was added. A portion of each solution was transferred to a flattened glass capillary (8 mm (i.d.) × 0.8 mm (i.d.) × 30 mm; transmittance cutoff 300 nm; Vitrocom) and flame-sealed after being degassed by four freeze–pump–thaw cycles at $<10^{-5}$ Torr on a mercury-free vacuum line.

Another portion of each solution from the separated extract was deposited on a Pike Technologies Miracle™ single reflection HATR. Infrared spectra of the material, after allowing time for solvent evaporation, were obtained by summing 500 scans using a Perkin–Elmer Spectrum One infrared spectrometer.

2.5. Steady-state fluorescence

Fluorescence excitation (corrected for detector response) and emission spectra (uncorrected) under vacuum ($<10^{-5}$ Torr) were recorded at a right-angle from the back-faces of films on a Spex Fluorolog 111 spectrofluorimeter with a 150-W high-pressure xenon lamp and 0.25 mm (ca. 0.9 nm resolution) slit widths on both the excitation and emission monochromators.

2.6. Differential scanning calorimetry

DSC analyses were performed using a TA2910 DSC cell base interfaced to a Thermal Analyst 3100 controller. The

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[2] The number in the acronym names for the PE films refers to the percent of crystallinity from X-ray determinations (vide infra).

apparatus was calibrated with an indium standard. Samples were placed in crimped aluminum pans and heated at 10 °C/min. under a slow stream of nitrogen. The cooling rate was uncontrolled and depended on the difference between ambient and sample cell temperatures. Crystallinity contents in films were calculated from powder X-ray diffractograms recorded on a Rigaku R-AXIS image plate system using Cu Kα radiation ($\lambda = 1.54056$ Å). Data were processed and analyzed using MDI-Jade (version 5) software. Crystallinities from X-ray analyses differ from the DSC values [10] and are much more reproducible. Although both sets of data are reported in Table 1, the X-ray values are used to compare different film types.

2.7. Treatment of fluorescence decay data

Fluorescence decay histograms were recorded on an Edinburgh Analytical Instruments model FL900 time-correlated single photon counting system using H_2 as the lamp gas. Films in evacuated ($<10^{-5}$ Torr) flattened quartz capillaries were aligned at ~45° to the incident radiation. Emission was detected at a right angle from the back-face of the sample. An instrument response function was determined using Ludox as scatterer and without polarizers. Data were collected in 1023 channels (0.504 ns/channel), and $\sim 10^4$ counts were collected in the peak channel (beyond the scatter peak, if present) unless indicated otherwise.

A range from time zero (a channel before the onset of the instrument-response-signal) to at least two decades of decay from the peak channel was included in the analyses. Curves were deconvoluted and fitted to functions with a nonlinear least-squares routine supplied by Edinburgh Instruments. A small 'scatter peak' of very short duration was present in the decay profiles of some of the films. Each is omitted from reported fits but has been included in the analyses of histograms. When $\chi^2 < 1.2$ and no systematic deviation was apparent in plots of residuals, fits were deemed acceptable. Initially, monoexponential fits were attempted. If unacceptable for either reason above, two exponential terms and so on were used until satisfactory fits were achieved.

3. Results

3.1. Criteria for attachment selectivity

Lamotte and co-workers [11,12] have shown that ultraviolet irradiation of pyrene in solid and liquid alkane solutions yields 1-alkylpyrenes in addition to other photoproducts whose number and type depend on photon wavelength. The 1-position of ground-state pyrene is known to be the most reactive toward radicals (and cations) [13,14], and ab initio calculations indicate that it is also the most reactive site of the first excited singlet state [15]. Photoreactions of pyrene in very polar, protic media are known to produce at least two photoproducts [16–18]. We have also demonstrated that >300 nm radiation can lead to attachment of pyrene to chains of PE films [1]. In *n*-alkane matrices, the mode of attachment is very dependent on solvent phase, pyrene concentration, radiation wavelength, and alkane chain length; pyrene molecules reside and react preferentially at interfaces between lamellae in solid phases of long-chained *n*-alkanes [15].

Here, the attachment selectivity of pyrene to chains of PE is based on several dynamic and spectroscopic signatures of irradiated (and exhaustively extracted) films. They include the position and shape of UV/Vis absorption and excitation/emission spectra (NB: the spectra of 1-ethylpyrene and other 1-alkylated pyrenes are bathochromically shifted by ~7 nm relative to spectra of pyrene [1]) and singlet lifetimes (e.g. the singlet lifetime of 1-ethypyrene in PE, ca. 194 ns [19], is significantly shorter than that of pyrene, ca. 300 ns [19]). Attachment selectivity is considered to be best when the excitation and emission spectra of the attached lumophores are not wavelength dependent and have the same shape, position, and temporal decay characteristics as 1-alkylated pyrenes [19].

3.2. Irradiations of films under different atmospheres

Figs. 1 and 2 show the emission (λ_{ex} 343 nm) and excitation spectra (λ_{em} 377 nm) of 10^{-2} mol/kg pyrene in PE37 films containing various amounts of erucamide (PE37-*n*, where *n* = ca. 5 or 10 wt% erucamide) that have been irradiated either under a nitrogen atmosphere (n-PE37-*n*), air (a-PE37-*n*), or vacuum (v-PE37-*n*). The shapes of the emission and excitation spectra suggest that the selectivity of pyrene attachment increases in the order: v-PE37 > n-PE37 > a-PE37. The concentration of molecular oxygen in a-PE37 films, ca. 3.7×10^{-3} mol/kg [20–22], is much higher than in the n-PE37 and v-PE37 films. As a result, molecular oxygen contributes least to pyrenyl-related processes in the latter two films. Its influence on attachment selectivity is discernible in the

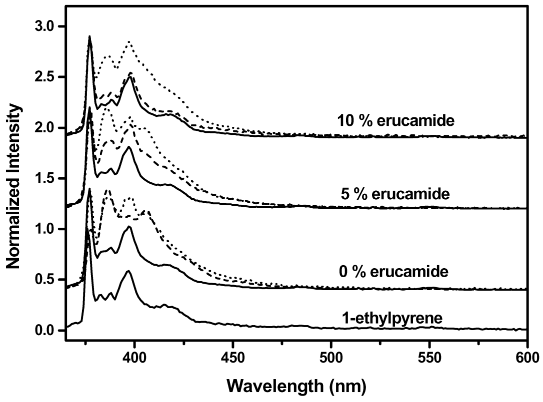


Fig. 1. Fluorescence spectra (λ_{ex} 343 nm) of UV-irradiated (for 1 h) 10^{-2} mol/kg pyrene in v-PE37 (—), *n*-P37 (- - -) and a-PE37 (···) films of varying erucamide content and of 10^{-6} mol/kg 1-ethylpyrene in PE42. All spectra are recorded in vacuo.

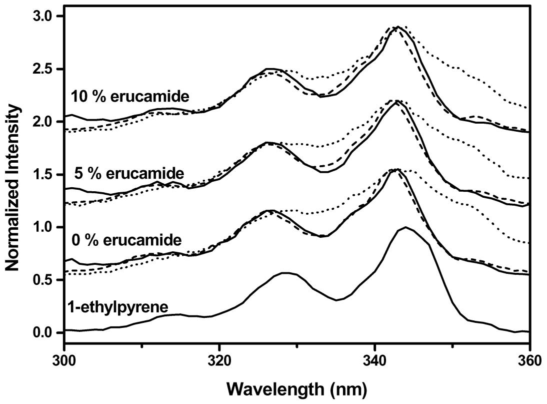


Fig. 2. Excitation spectra (λ_{em} 377 nm) of UV-irradiated (for 1 h) 10^{-2} mol/kg pyrene in v-PE37 (—), n-PE37 (- - -), and a-PE37 (···) films of varying erucamide content and of 10^{-6} mol/kg 1-ethylpyrene in PE42. All spectra are recorded in vacuo.

changes in relative intensities and the degree of band broadening of the peaks at 386 and 398 nm in the emission spectra and the appearance or absence of a peak at ~360 nm in the excitation spectra.

The fluorescence decay histograms of v-PE37 films (i.e. containing no erucamide; Table 2) are nearly mono-exponential and the lifetimes of the major decay component, τ_1, (~190 ns) are very similar to that of 1-ethylpyrene in PE37 [19]. The fluorescence decay component of intermediate duration, τ_2, may be due to attached pyrenyl groups that are aggregated in the ground state. A variety of orientations, some not optimal for a classical excimer formation, probably are present and shift emissions to longer wavelengths [23]; some of the aggregate emission may be under the structured, stronger emission of the monomer [19]. We attribute the shortest component, τ_3, to species derived from PE37 upon irradiation. Although emission from undoped, irradiated v-PE37 films is weak, the majority of it has decay times like τ_3, and the remainder is from a species whose emission spectrum is also not pyrenyl-like.

Table 2
Time resolved fluorescence data (λ_{ex} 343 nm) from erucamide-doped v-PE37 films with attached 1-pyrenyl groups

λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2
0% Erucamide				
377	195.0 ± 0.5(94)	26.9 ± 0.9(4)	0.4 ± 0.1(2)	1.166
398	194.6 ± 0.5(90)	20.9 ± 0.4(8)	0.4 ± 0.1(2)	1.164
415	193.4 ± 0.5(87)	19.0 ± 0.3(10)	0.6 ± 0.1(3)	1.266
424	193.3 ± 0.5(89)	19.4 ± 0.4(8)	0.4 ± 0.1(3)	1.168
5% Erucamide				
377	200.9 ± 0.5(94)	37.3 ± 1.3(5)	0.5 ± 0.1(1)	1.506
398	193.7 ± 0.5(92)	20.8 ± 0.5(6)	0.4 ± 0.1(2)	1.062
415	197.8 ± 0.5(89)	21.4 ± 0.4(8)	0.8 ± 0.1(3)	1.532
424	198.7 ± 0.5(90)	21.4 ± 0.4(7)	0.7 ± 0.1(3)	1.597
10% Erucamide				
377	193.8 ± 0.4(98)	20.4 ± 1.5(2)	–	1.324
398	194.6 ± 0.4(97)	20.0 ± 0.9(3)	–	1.187
415	194.4 ± 0.4(96)	17.9 ± 0.6(4)	–	1.180
424	194.9 ± 0.4(96)	17.7 ± 0.6(4)	–	1.159
377[a]	194.0 ± 0.4(100)	–	–	1.095

Relative percentages of each decay component are in parentheses.

[a] 10^{-6} mol/kg 1-ethylpyrene in PE42; in vacuo [19].

Emission (λ_{ex} 343 nm) and excitation (λ_{em} 377 nm) spectra from a-PE37-0 and n-PE37-0 films did not resemble closely those of 1-ethylpyrene (Figs. 1 and 2). The shapes and positions of the excitation spectra were dependent on emission wavelength; they shifted bathochromically as the emission wavelength was increased. The tri-exponentiality of the fluorescence decays (Appendix C: Tables C1 and C2) and the wavelength dependence of the excitation spectra suggest the presence of more than one emitting species. However, the τ_1 components for n-PE37-0 and a-PE37-0 films, ca. 190 ns, indicate that they emanate from 1-alkylpyrenyl groups attached to the polymer chains.

We suggest that the species responsible for the τ_2 decay component is formed from reactions between residual oxygen molecules and excited-state, attached 1-pyrenyl groups or their intermediates (vide infra), while the short τ_3 component may be formed by photo-oxidations of PE37. They are not from reaction between pyrenyl moieties and traces of chloroform that could have been present in the films after doping: films doped with hexane solutions of pyrene and then irradiated under vacuum produced emission spectra and fluorescence decays like those from chloroform-treated films (see Appendix B). However, the excitation spectra (λ_{em} 377 nm) of the v-PE37, n-PE37, and a-PE37 films with attached 1-pyrenyl groups exhibit a peak at ca. 354 nm that is not from a 1-alkylpyrenyl moiety. It is most pronounced in the excitation spectrum from the a-PE37 film (Fig. 2). At λ_{ex} 354 nm, emission spectra from a-PE37 and n-PE37 films are unlike that from the v-PE37 film (Fig. 3) and lack a strong emission peak at 376 nm characteristic of a 1-alkylpyrenyl group [24]. Only traces of emissions not ascribable to 1-pyrenyl groups (characterized by decreased intensity of the 376 nm band relative to the peaks at ~386 and 405 nm) are detectable in v-PE37 films.

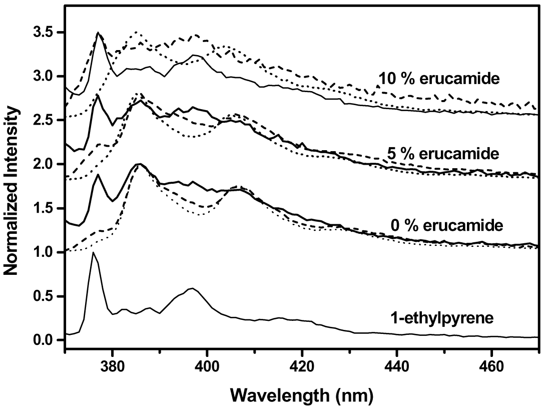


Fig. 3. Emission spectra (λ_{ex} 354 nm) of UV-irradiated 10^{-2} mol/kg pyrene in v-PE37 (—), n-PE37 (- - -), and a-PE37 (···) films of varying erucamide content and of 10^{-6} mol/kg 1-ethylpyrene in PE42. All spectra are recorded in vacuo.

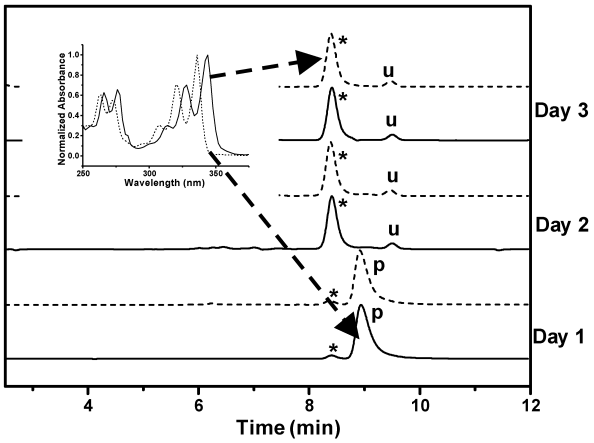


Fig. 4. GPC (THF; λ_{det} 343 nm) chromatograms of extracts from v-PE37-0 (—) and v-PE37-10 (- - -) films. Peaks labeled with 'p' and an asterisk have UV/Vis absorption spectra like that of pyrene and a 1-alkylated pyrene, respectively. The peaks at 9.4 min labelled with 'u' lack the vibronic structure associated with a polycyclic aromatic molecule. Inset: UV/Vis absorption spectra of peaks with 8.5 (—) and 9.0 (- - -) min retention times.

3.3. Influence of erucamide on the course of irradiations of v-PE37, n-PE37, and a-PE37

Molecules of pyrene that became attached to erucamide instead of polyethylene chains could be removed from films by the washing procedures. GPC chromatograms (λ_{det} 343 nm) of the condensed extracts from v-PE37-0 and v-PE37-10 films and UV/Vis spectra of the peaks are presented in Fig. 4. Pyrene (~9.00 min retention volume) is the dominant species in extracts collected after the first 24 h of film immersion; only traces of 1-alkylpyrenyl species (~8.5 min retention volume) are detected. Chromatograms of extracts collected on the second and third days of film immersion indicate the presence of only 1-alkylpyrenyl species (~8.5 min retention volume) whose nature appears to be similar regardless of the presence or absence of erucamide in the irradiated films. A peak of unknown origin at ~9.5 min whose absorption spectrum lacks the vibronic structure associated with a polycyclic aromatic molecule is present in second and third day extracts. However, there are some distinct differences between both the steady-state and time-resolved fluorescence characteristics of extracts from the two films. Excitation and emission spectra (Fig. 5) of the day-three extract from the v-PE37-0 film and 1-ethylpyrene are superimposable and their decay constants in hexane are similar: $\tau_1^{\text{v-PE37-0}} \sim 225$ ns; $\tau_1^{\text{1-ethylpyrene}} \sim 260$ ns. The excitation spectrum of the day-three extract from the v-PE37-10 film is blue-shifted and the emission spectrum is slightly red-shifted relative to those of 1-ethylpyrene; the decay constant, $\tau_1^{\text{v-PE37-10}} = \sim 150$ ns (Fig. 6), is significantly shorter than that of 1-ethylpyrene. These data suggest that pyrene and erucamide molecules can occupy the same parts of polyethylene films and that, upon irradiation, they undergo intermolecular reactions (steps 11–14 of Scheme 2) in competition with attachment of pyrene to polyethylene chains. In the absence of erucamide, irradiated pyrene molecules become attached to a greater degree to polyethylene chains, but some of the photoreactions lead to attachment to short paraffin chains (as a result of radiation induced cleavage of long chains; step 7 of Scheme 1).

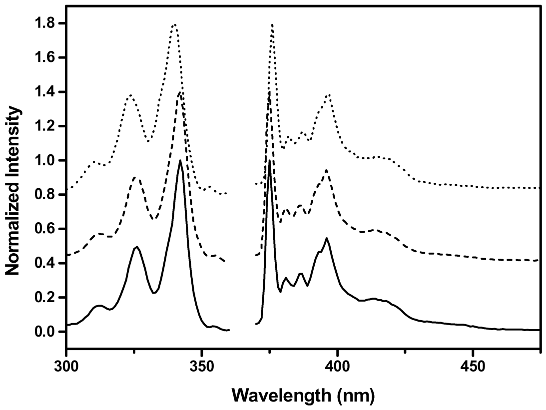


Fig. 5. Excitation (λ_{em} 377 nm) and emission (λ_{ex} 343 nm) spectra of day-three extracts from v-PE37-0 (- - -) and v-PE37-10 (···) films and of 10^{-6} M 1-ethylpyrene (–) in degassed hexane.

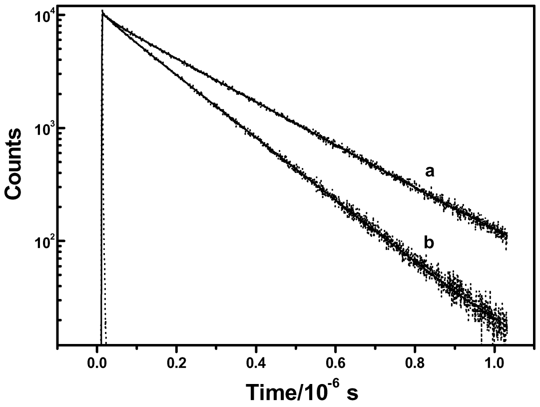


Fig. 6. Semilog plot of the time-resolved emission intensity (λ_{ex} 343 nm, λ_{em} 377 nm) of day-three extracts from (a) v-PE37-0 and (b) v-PE37-10 films in degassed hexane. The lamp profile is also included.

Infrared spectra of the 8.5 min retention volume peak from extracts of the irradiated v-PE37-10 film, as well as from erucamide and 1-ethyplyrene, are shown in Fig. 7. Although the IR spectra of the extracted peak and erucamide

$$\text{PyH} \xrightarrow[(>300\text{ nm})]{h\upsilon} {}^1\text{PyH} \quad (2)$$

$$ {}^1\text{PyH} \xrightarrow{\text{ISC}} {}^3\text{PyH} \quad (3)$$

$$ {}^3\text{PyH} \xrightarrow{h\upsilon} {}^3\text{PyH}^* \quad (4)$$

$$\text{H-R-R-H} + {}^3\text{PyH}^* \longrightarrow \text{H-R-R-H}^* + \text{PyH} \quad (5)$$

$$\text{H-R-R-H}^* \longrightarrow \text{H-R-R}\bullet + \text{H}\bullet \text{ or } 2\ \text{H-R}\bullet \quad (6)$$

$$\text{H-R-R}\bullet \text{ or } \text{HR}\bullet + \text{PyH} \longrightarrow \text{HR-PyH}\bullet \text{ or } \text{H-R-R-PyH}\bullet \quad (7)$$

$$\text{H}\bullet + \text{PyH} \longrightarrow \text{H-Py-H}\bullet \xrightarrow{[\text{H}\bullet]} \text{PyH}_3 \quad (8)$$

$$\text{HR-Py-H}\bullet \xrightarrow{-[\text{H}\bullet]} \text{HR-Py} \quad (9)$$

$$\text{H-R-R-PyH}\bullet \xrightarrow{-[\text{H}\bullet]} \text{H-R-R-Py} \quad (10)$$

Scheme 1. Proposed mechanism for attachment of pyrene (PyH) to polyethylene using UV/Vis radiation in the absence of oxygen and erucamide. H–R–R–H represents a polyethylene chain.

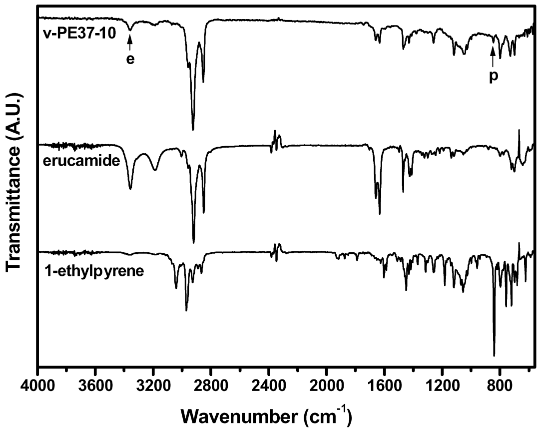


Fig. 7. Infrared spectra of ~8.5 min retention volume peak of solution extracted on day 3 from irradiated v-PE37-10 film, as well as infrared spectra of 1-ethypyrene and erucamide. Intensities of peaks labelled ‘e’ and ‘p’ were scaled to construct an infrared spectrum approximating a 1:1 erucamide/pyrene adduct; see text for details.

are very similar, their structures must be quite different because the 8.5 min peak exhibits fluorescence of a 1-alkylated pyrene (see above). Erucamide (retention volume ~6.0 min) is easily separated from the 8.5 min peak and reinjection of the collected 8.5 min peak shows no evidence for contamination by erucamide. These data indicate that pyrene can be covalently linked to erucamide as well as to the polyethylene matrix and that the weakness of the pyrenyl-associated band in the infrared spectrum of the 8.5 min peak is a true reflection of the functional group composition within the molecule(s) (Fig. 7). There is ample precedence for attachment of pyrene to alkyl chains like that of erucamide [1].

Other species that lack chromophores absorbing in the 220–400 nm range, perhaps PE-based fragments [25], may have co-eluted with the ~8.5 min peak. Bands associated with the infrared absorption of an alkylated pyrene are very weak in Fig. 7 or are overlapped by stronger, erucamide-derived bands. The v-PE37-10 spectrum in Fig. 7 was not reproduced entirely by adding the spectra of erucamide and 1-ethylpyrene (as normalized on the bases of the relative intensities of the peaks at 840 cm^{-1} (associated uniquely with alkylated pyrene groups) and 3360 cm^{-1} (due to the amide in erucamide)). It failed to account for the large peak intensities in the C–H stretching region (NB: bands between 3048 and 2800 cm^{-1}; see Appendix C).

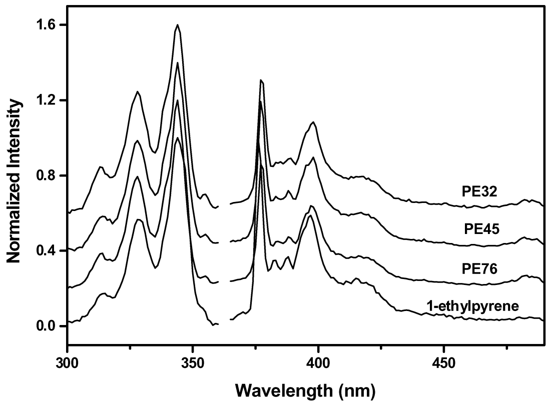


Fig. 8. Excitation (λ_{em} 377 nm) and emission (λ_{ex} 343 nm) spectra of pyrene doped PE films after UV irradiation (>300 nm) under vacuum ($<10^{-5}$ Torr) and of 10^{-6} mol/kg 1-ethylpyrene in PE42. All spectra are recorded in vacuo.

The selectivity of pyrene attachment increases with the concentration of erucamide in PE37 films irradiated under each type of atmosphere. Emission from the non 1-pyrenyl species (NB: at 386 and 405 nm) is most prominent when λ_{ex} is 354 nm and in films containing no erucamide (Fig. 3); more erucamide increases attachment selectivity. This trend is also evident in the fluorescence decay histograms of v-PE37-10, n-PE37-10, and a-PE37-10 films. The greatest selectivity is seen in the v-PE37-10 film whose fluorescence decay histogram can be fit well to a bi-exponential function in which the τ_1 component is dominant (Table 2).

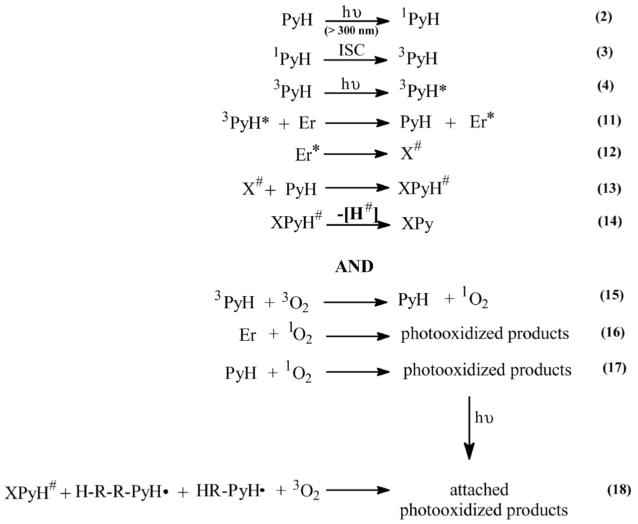
3.4. Influence of PE crystallinity

Emission and excitation spectra of 10^{-2} mol/kg pyrene-doped PE films of varying crystallinity that were irradiated under vacuum are shown in Fig. 8. Their spectra are almost superimposable on that of 1-ethylpyrene doped in PE. The fluorescence decay data for all of the films are nearly mono-exponential and the lifetimes of the major decay component, τ_1, (~190 ns) are very similar to that of 1-ethylpyrene in PE37 (see Appendix C, Table C3) [19]. Thus, selectivity of pyrene attachment does not depend on PE film crystallinity, at least within the range examined, when irradiations are conducted in vacuo, under nitrogen, or in air.

4. Discussion

4.1. Mechanism of UV attachment of pyrene

The proposed mechanism for attachment of pyrene initiated by UV photons ($\lambda \geq 300$ nm) in the absence of molecular oxygen and erucamide is presented in Scheme 1 [15]. Overall, the mechanism requires sequential absorption of two photons by each pyrene molecule for attachment to occur. At these wavelengths, pyrene chromophores are excited selectively in the sea of non-absorbing C–H and C–C bonds from polyethylene. The vertical ionization potential of pyrene (gas phase) is ca. 6.2 eV [26]. Thus, excitations with ≥300 nm photons (<5.1 eV) yield low-lying excited singlet states (^{1}PyH) that can undergo intersystem crossing to the longer-lived lowest triplet state (^{3}PyH; $\Phi_{ST} = 0.37$ and $\tau_T = 180$ μs at 25 °C in cyclohexane [27]), and subsequently absorb another photon under the high flux conditions employed [11,12,15,16]. These highly energetic triplet states (^{3}PyH*) initiate the photochemistry of attachment by transferring their excitation energy to neighboring polyethylene chains (H–R–R–H) that



Scheme 2. Proposed mechanism for attachment of pyrene (PyH) to polyethylene using UV/Vis radiation in the presence of oxygen and erucamide (Er). H–R–R–H represents a polyethylene chain. $X^{\#}$ is an intermediate of unknown structure generated from erucamide; its attachment product to pyrene is extractable from the films.

dissociate to radicals via C–H (H–R) or C–C (R–R) bond cleavage (steps 6 and 7) [11,12]. The alkyl radicals can add efficiently to their (ground-state) pyrene donor molecules because diffusion in PE films is slow. Attached 1-alkylpyrenyl groups result when a (putative) H• atom is lost from the initial adduct (steps 9 and 10).

Additional pathways are possible if traces of rapidly diffusing molecular oxygen ($^3O_2$) are present within the films at the time of irradiation (Scheme 2) [28]. Energy transfer from ^{3}PyH may lead to $^1O_2$ via competitive energy transfer, a one-photon process (step 15 in Scheme 2). $^1O_2$ can react with ground-state pyrene to form photo-oxidized pyrenyl products (step 17) that then add to PE chains or $^1O_2$ can interact with intermediates generated in Scheme 1 (step 7). Both processes are feasible since pyrene [29] and molecular oxygen [30] most likely reside within the amorphous and interfacial (i.e. along the lateral faces of crystallites) regions of PE films. Nitrogen purging removes most, but not all, of the oxygen absorbed in PE films.

We suggest that erucamide may acts as a $^1O_2$ scavenger. Amides are known to be photooxidized readily [31] and the double bond of erucamide can undergo the classical 'ene' reaction with $^1O_2$ [32,33]. In semicrystalline polymers such as polyethylene, erucamide resides in the amorphous and interfacial regions, also [34], where it can interact easily with pyrene and molecular oxygen. Since the bulk concentration of erucamide is much larger than that of pyrene even at the lowest added concentration (i.e. in PE37-5), reaction between erucamide and $^1O_2$ is favored statistically. Erucamide intercepts $^1O_2$ (step 16) and possibly PE-derived intermediates that produce non-pyrenyl lumophores. By scavenging $^1O_2$, erucamide allows pyrene molecules or their intermediates a greater opportunity to undergo steps 8–10 of Scheme 1.

5. Conclusions

Pyrene-doped films that are irradiated in air or after being purged with nitrogen result in attachment of 1-pyrenyl as well as larger amounts of other species that are presumably from photo-oxidation processes. When irradiations are conducted on pyrene-doped films in vacuo, there is no apparent dependence of attachment selectivity on polymer crystallinity.

Erucamide appears to scavenge $^1O_2$ (and other $^3O_2$ derived species), allowing pyrene molecules to follow Scheme 1 without major intervention of Scheme 2. Erucamide also appears to scavenge non-oxygen containing species; attachment selectivity increases with erucamide content in films that have been irradiated in vacuo, under nitrogen atmospheres, or in air.

Pyrene and erucamide molecules occupy the same parts of polyethylene films and upon irradiation, undergo intermolecular reactions in competition with attachment of pyrene to polyethylene chains. In the absence of erucamide, pyrene molecules become attached to a greater degree to polyethylene chains, but some of the photoreactions lead to attachment to short paraffin chains as a result of radiation-induced cleavage of long chains.

Very selective attachment of pyrene to polyethylene chains in films can be achieved using relatively low energy radiation (>300 nm) when samples are thoroughly degassed. Polyethylene films with attached 1-pyrenyl groups as the dominant fluorescing species should be more sensitive and more accurate probes of macro perturbations to polyethylene and other polyolefinic films, such as temperature changes and cold-stretching [2,35]. The 'recipe' presented here for 'clean attachment' of 1-pyrenyl lumophores is applicable to a wide variety of polyolefinic materials [35]. They should simplify interpretations of micromorphological changes caused by macroscopic perturbations.

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Appendix A

See Fig. A1.

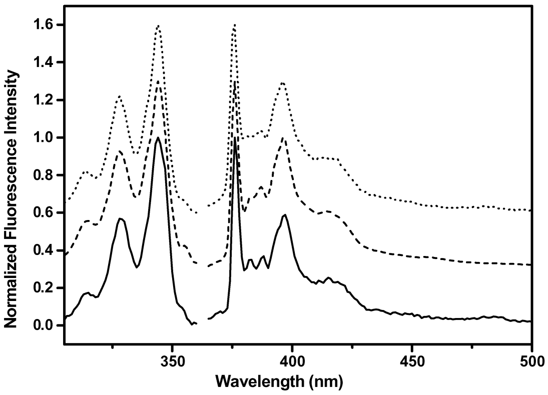

Fig. A1. Excitation (λ_{em} 377 nm) and emission (λ_{ex} 343 nm) spectra of pyrene derivatized PE42 films (irradiated under vacuum) using chloroform (···) and hexane (- - -) doping procedures and 10^{-6} mol/kg 1-ethylpyrene in PE42 (—).

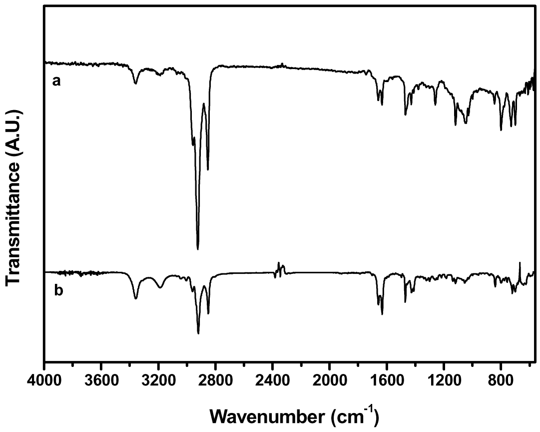

Fig. B1. Infrared spectra of 8.5 min retention volume component from day 3 extract of v-PE37-10 film (a) and (b) sum of erucamide and 1-ethylpyrene spectra scaled to match the intensities at 3360 cm^{-1} (erucamide) and 840 cm^{-1} (1-ethylpyrene) in (a).

Table C1
Time resolved fluorescence data (λ_{ex} 343 nm) from erucamide-doped n-PE37 films with attached 1-pyrenyl groups

λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2
0% Erucamide				
377	169.2 ± 2.8(58)	20.4 ± 0.7(24)	6.6 ± 0.2(15)	1.062
398	160.5 ± 2.6(47)	20.1 ± 0.4(40)	6.8 ± 0.3(12)	1.074
415	154.6 ± 2.6(43)	20.8 ± 0.4(44)	6.3 ± 0.3(12)	1.073
424	162.5 ± 2.9(46)	21.2 ± 0.4(38)	6.4 ± 0.2(15)	1.174
5% Erucamide				
377	171.1 ± 2.3(65)	18.9 ± 0.6(21)	6.0 ± 0.3(11)	1.142
398	170.2 ± 2.4(57)	22.2 ± 0.6(28)	7.4 ± 0.3(14)	1.157
415	162.2 ± 2.1(55)	20.2 ± 0.3(33)	5.4 ± 0.2(11)	1.148
424	164.1 ± 2.3(55)	19.8 ± 0.4(29)	5.5 ± 0.2(13)	1.150
10% Erucamide				
377	177.2 ± 2.0(73)	19.6 ± 1.1(13)	7.1 ± 0.2(13)	1.148
398	179.0 ± 1.7(80)	21.9 ± 1.1(11)	6.8 ± 0.3(8)	1.265
415	174.6 ± 1.5(78)	19.1 ± 0.5(14)	4.7 ± 0.2(7)	1.124
424	174.2 ± 1.6(77)	18.7 ± 0.6(13)	4.8 ± 0.2(8)	1.196
377[a]	194.0 ± 0.4(100)	–	–	1.095

Relative percentages of each decay component are in parentheses.
[a] 10^{-6} mol/kg 1-ethylpyrene in PE42; in vacuo [19].

Table C2
Time resolved fluorescence data (λ_{ex} 343 nm) from erucamide-doped a-PE37 films with attached 1-pyrenyl groups

λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2
0% Erucamide				
377	187.7 ± 1.0(58)	32.0 ± 0.6(31)	8.5 ± 0.3(11)	1.149
386	184.1 ± 1.4(44)	31.2 ± 1.0(36)	12.5 ± 0.5(20)	1.076
406	188.7 ± 1.7(38)	33.0 ± 1.0(34)	12.4 ± 0.3(28)	1.195
424	190.5 ± 1.7(35)	30.7 ± 0.8(36)	11.1 ± 0.3(29)	1.162
5% Erucamide				
377	194.7 ± 1.4(62)	43.6 ± 1.4(24)	12.0 ± 0.4(13)	1.150
386	190.8 ± 2.3(47)	50.2 ± 3.5(19)	17.5 ± 0.4(33)	1.070
406	184.0 ± 1.5(46)	34.4 ± 1.4(28)	13.0 ± 0.4(25)	1.039
424	187.7 ± 1.6(43)	34.8 ± 1.1(28)	11.7 ± 0.3(27)	1.141
10% Erucamide				
377	187.1 ± 1.4(70)	51.3 ± 2.2(20)	14.2 ± 0.6(9)	1.108
386	182.8 ± 1.8(49)	44.5 ± 2.1(24)	15.1 ± 0.4(26)	1.106
406	184.1 ± 1.6(50)	42.7 ± 1.6(26)	13.6 ± 0.3(23)	1.154
424	183.0 ± 1.3(55)	37.6 ± 1.1(26)	10.1 ± 0.3(17)	1.122
377[a]	194.0 ± 0.4(100)	–	–	1.095

Relative percentages of each decay component are in parentheses.
[a] 10^{-6} mol/kg 1-ethylpyrene in PE42; in vacuo [19].

Appendix B

See Fig. B1.

Appendix C

See Tables C1–C3.

Table C3
Time resolved fluorescence data (λ_{ex} 343 nm) from various crystallinity PE films with attached 1-pyrenyl groups

λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2
PE32				
377	186.2 ± 1.3(85)	11.2 ± 0.2(11)	1.5 ± 0.1(4)	1.176
398	184.9 ± 1.1(88)	12.7 ± 0.2(9)	1.9 ± 0.1(3)	1.128
415	195.8 ± 1.7(88)	20.5 ± 1.0(9)	5.3 ± 0.3(3)	1.217
424	191.3 ± 1.4(89)	18.1 ± 0.8(7)	4.6 ± 0.3(4)	1.153
PE45				
377	174.2 ± 1.1(86)	11.7 ± 0.2(12)	0.9 ± 0.1(3)	1.255
398	184.8 ± 1.4(82)	17.0 ± 0.3(16)	3.5 ± 0.2(3)	1.204
415	178.3 ± 1.5(79)	16.6 ± 0.3(18)	2.8 ± 0.1(3)	1.131
424	178.7 ± 1.4(80)	16.0 ± 0.2(17)	2.3 ± 0.1(4)	1.082
PE76				
377	173.9 ± 1.5(78)	12.6 ± 0.3(12)	2.3 ± 0.1(6)	1.243
398	175.4 ± 1.2(86)	13.7 ± 0.3(10)	2.2 ± 0.1(3)	1.321
415	175.7 ± 1.3(84)	14.6 ± 0.4(10)	2.6 ± 0.1(4)	1.110
424	177.7 ± 1.3(83)	15.1 ± 0.4(9)	2.6 ± 0.1(4)	1.284
377[a]	194.0 ± 0.3(100)	–	–	1.095

Relative percentages of each decay component are in parentheses.
[a] 10^{-6} mol/kg 1-ethylpyrene in PE42; in vacuo [19].

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