Method for Hydroxylation and Esterification of Interior Sites of Polyolefinic Films

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ABSTRACT: A method is described to functionalize specifically the interior portions of polyolefinic films with chromophoric/lumophoric groups. In the first step, a film doped with dibenzothiophene 5-oxide (DBTO) is irradiated (λ > 300 nm) to produce O(^{3}P) atoms that oxidize nearby C−H bonds of the polymer. Covalent attachment of acid chlorides (containing chromophoric/lumophoric groups) to the hydroxy bonds (via ester linkages) provides films that retain their absorption and luminescence in water or air for long periods. The esterified films have been characterized using UV/vis absorption spectroscopy and static and dynamic fluorescence techniques. Fluorescence from native or modified and then esterified films in 1.0 M methanolic 2-(dimethylamino)ethanol, a surface quencher, indicates that the vast majority of the chromophores/lumophores are located inside the films. Selective modification of the film surfaces by an analogous method was not efficient. However, a very low concentration of hydroxy groups is present throughout the native films. Their esterification reduces the fluorescence contrast between undoped/irradiated and DBTO-doped/irradiated parts of a film.

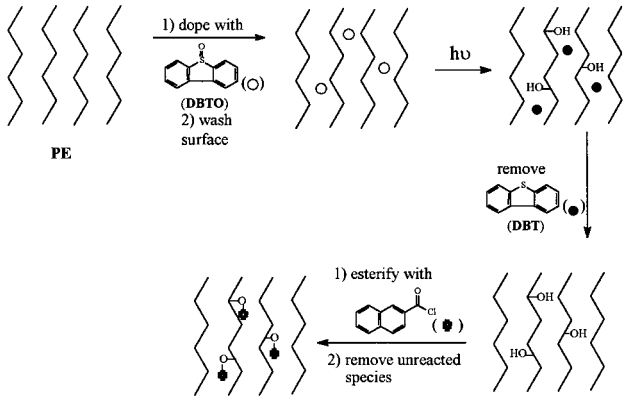
Introduction

The physical and chemical properties of polyolefins and polyethylene, in particular, make these materials useful in a broad range of commercial applications. However, owing to their hydrophobicity and relatively unreactive nature, their surfaces are less adhesive and less wetting than is necessary for some purposes.[1] To overcome this problem, several methods have been developed to *modify specifically the surfaces* of polyolefinic films.[2] They include grafting,[3] layer-by-layer depositions,[4] surface blending,[5] and oxidations by plasmas,[6,7] corona discharges,[7] flames,[8] UV−vis irradiations,[9] or chemicals.[10] Polar groups physically or chemically attached to the film surfaces as a consequence of or subsequent to these modification procedures are usually very prone to loss in the environment by hydrolysis or contact with light and large concentrations of atmospheric oxygen. Other blending methods, copolymerizations, and deeper UV irradiations of oxygen-perfused polymers[11] place easily modifiable functional groups *indiscriminately at surface and interior sites* of a film.

We are unaware of a method to *modify interior sites of polyolefinic films* so that a large variety of groups can be attached subsequently. Previously, we have reported two rather *specific* methods for interior attachment to interior sites of polyolefinic films: 1-pyrenyl groups can be introduced by irradiation of pyrene[12] and 9-anthrylmethyl groups can be attached by thermolysis or heating (9-anthryl)diazomethane.[13]

Here, we report the development of a method for interior attachment and apply it to two different polyethylene films.[14] Groups linked to polymer chains in this way are not lost by abrasion or upon submersion of films in water for protracted periods (currently greater than 100 days). They should also be more resistant to loss by contact with air and light than those attached to surfaces. Analogous techniques lead to covalent attachment of groups primarily[14] to film surfaces but much less efficiently than in the interior. Our approach is outlined in Scheme 1.

Scheme 1. Cartoon Representation of the Method for Interior Modification and Derivatization of the Amorphous Regions of Polyethylene Films



Experimental Section

Instrumentation. Melting points were measured on a Leitz-Wetzlar microscope equipped with a Leitz 585 thermostating unit and an Omega microprocessor thermocouple. FT-IR spectra were recorded on a MIDAC spectrophotometer. Attenuated total reflectance (ATR) IR spectra were recorded with a Nicolet Magna-IR 750-II spectrometer equipped with a model 300 continuously variable ATR accessory from Spectra-Tech. A Varian mercury 300 MHz NMR spectrometer connected to a Sun Sparcstation computer was used to record ^{1}H NMR spectra. The solvent was $CDCl_3$, and TMS was the internal standard. Differential scanning calorimetry (DSC) was performed on a TA 2910 differential scanning calorimeter interfaced to a TA Thermal Analyst 3100 controller. Samples (ca. 2.5 mg) of film in open aluminum pans were heated (5 °C/min) under a slow stream of nitrogen. HPLC analyses were carried out on a Gilson model 116 instrument equipped with a silica gel column (IBM, 4.6 mm × 250 mm) and a UV detector (254 nm) and on a Spectra-Physics instrument equipped with a silica gel column (Waters, 3.9 mm × 150 mm) and a Waters Associates model 440 UV absorbance detector (254 nm). UV−vis absorption spectra were recorded on a HP8452A diode array spectrophotometer or a Perkin-Elmer Lambda-6 UV−vis spectrophotometer. Spectra of modified/esterified films were referenced to a native unmodified film, but unbalanced

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scatter from film surfaces sometimes resulted in baselines with high apparent optical densities. A Spex 111 Fluorolog fluorometer (150W Osram XBO xenon lamp) interfaced with an ACCEL 486 computer was used to record fluorescence and excitation spectra. Films were placed at a ca. 45° angle to the exciting beam, and fluorescence was measured from the backside of the film at ca. 45° (total right-angle geometry). Excitation spectra were corrected for detector response.

Contact angles of droplets on film surfaces were measured on a Ramé-Hart goniometer and an AST Products VCA 2500XE video contact angle system using doubly distilled water delivered by a motorized syringe. Films were held flat with a clamp. The data reported are averages of at least five readings at different positions on a film surface.

Fluorescence decays were determined with an Edinburgh Analytical Instrument model FL900 time-correlated single photon counting system using H_2 as the lamp gas. A film was placed at a ca. 45° angle to the exciting beam in a quartz cell open to the air, and emission was detected at a right-angle geometry from the backface. "Instrument response functions" were recorded using Ludox as scatterer. No polarizing filters were used. Data were collected in 1023 channels, and at least 10^4 counts were collected in the peak channel. Deconvolution was performed by nonlinear least-squares routines, minimizing χ^2, with software supplied by Edinburgh. Initially, monoexponential fits were attempted followed by biexponential fits, etc. until $\chi^2 < 1.2$ and nonsystematic variations in residuals were achieved. Data were also analyzed using the global analysis method with software supplied by Edinburgh.

All spectroscopic measurements were carried out at ambient temperatures.

Materials. Solvents were HPLC grade and were used without further purification unless otherwise indicated. Low-density polyethylene films were NDLDPE (Sclair, 70 μm thick, 0.918 g/cm^3, 42% crystallinity) from Dupont of Canada and BLDPE (an additive-free blown-type film, 140 μm thick, 0.917 g/cm^3, 31% crystallinity, M_w = 510 000) from Poliolefinas of Brazil.[15] Prior to use, films were immersed in three batches of chloroform for 1 day each to remove antioxidants and impurities, rinsed in fresh methanol, and dried with a stream of nitrogen.

Dibenzothiophene 5-oxide (DBTO) was synthesized from dibenzothiophene (DBT; Aldrich, 95%) as described in the literature.[16] After purification by either recrystallization from hot benzene or column chromatography on silica gel (chloroform as eluent),[17] a white solid (90% yield; one peak by HPLC analysis), mp 192−194 °C (lit.[18] mp, 189−191 °C), was obtained. IR (KBr): 1025, 1067 cm^{-1}. ^{1}H NMR: δ (ppm) 7.5 (td, 2H), 7.6 (td, 2H), 7.8 (d, 2H), 8.0 (d, 2H). UV (hexanes): $\lambda_{max}(\epsilon)$ 250 (17100), 280 nm (7200). Ethyl 2-naphthoate (NAEt) was synthesized from 2-naphthoyl chloride (Aldrich, 98%) and ethanol in cold pyridine.[19] It was a colorless oil (one peak by HPLC analysis) after purification by column chromatography on silica gel (methylene chloride as eluent). IR ($CHCl_3$): 1713 cm^{-1}. ^{1}H NMR: δ (ppm) 1.4 (t, 3H, CH_3), 4.5 (q, 2H, CH_2), 7.5−7.6 (quintet of d, 2H, Ar−H), 7.9 (d, 2H, Ar−H), 8.0 (d, 1H, Ar−H), 8.1 (dd, 1H, Ar−H), 8.6 (s, 1H, Ar−H). UV (hexanes): $\lambda_{max}(\epsilon)$ 236 (59600), 271 (7700), 279 (8800), 288 (6500), 317 (1300), 332 nm (1400). 2-(Dimethylamino)ethanol (DMAE) was distilled, and the fraction with boiling point 133−134 °C was collected. Methanol was refluxed over magnesium metal for 2 h and then distilled.

Procedures for Interior Modification of Native Films and for Esterification of Native and Interior-Modified Films. Interior Modification. Typically, a 1 cm × 2 cm piece of cleaned PE film was immersed in a 0.4 M DBTO/chloroform solution for 24 h at 40 °C to reach ca. 18 or 15 mmol/kg dopant concentrations in the *amorphous* regions of NDLDPE or BLDPE, respectively. Concentrations (c, mol/kg) in the *amorphous* regions were calculated from UV absorption spectra and the equation $c = A_\lambda/(\epsilon_\lambda b\rho F)$; A_λ is the optical density at an appropriate wavelength (λ) averaged from five values obtained at different places on the film surface, ϵ_λ (M^{-1} cm^{-1}) is the molar extinction coefficient of DBTO in hexanes, b (cm) is the thickness of the film, ρ (g/cm^3) is the density of the film, and F is the fractional part of the film that is amorphous (i.e., noncrystalline). The film was rinsed in methanol to remove any DBTO on the film surfaces and dried with a stream of nitrogen. It was placed in a Pyrex test tube and deoxygenated by repeated evacuation−N_2 fill cycles. The test tube was irradiated for an equal period (15−20 min) on each side at a distance of 40−60 cm from an Oriel-6285 high-pressure Hg arc lamp operated at 400 W. The film was then immersed in chloroform aliquots until no absorption from DBTO or DBT could be detected in UV spectra of the last aliquot or the film.

In one experiment, the first three chloroform aliquots were collected and analyzed by HPLC: 73% of DBTO was converted to products, 96% of which was DBT. DSC traces of native, undoped and irradiated, and DBTO-doped and irradiated films were indistinguishable. Within the limits of detection, the various treatments do not lead to morphological changes in the films.

Esterification. A native film or one with a modified interior was placed in 5 mL of anhydrous chloroform (Aldrich, 99+%, stabilized with amylenes), 95 mg (0.5 mmol) of 2-naphthoyl chloride (Aldrich, 98%), 12 mg (0.1 mmol) of dimethylaminolpyridine (DMAP; Aldrich, 99%), and a few drops of dry pyridine. The mixture was stirred gently at 40 °C in a dry atmosphere for 1 week. After the third day, an additional 95 mg (0.5 mmol) of 2-naphthoyl chloride and 12 mg (0.1 mmol) of DMAP were added to the reaction mixture. The film was removed from the liquid and washed with chloroform and cyclohexane (alternating) in a Soxhlet extractor until the UV absorption and fluorescence spectra of the last aliquot showed no evidence of naphthyl-containing molecules. Concentrations of covalently attached naphthoate groups in the amorphous part of films were calculated by the equation above using ϵ_λ values for NAEt in hexanes.

Procedures for Surface Modification and Esterification of Native Films. Modification. The method above was employed except that films were dipped in a 25 mM DBTO/methanol solution[20] at room temperature for 20 s, dried horizontally, and irradiated on each side for 10 min. Surface-modified films for contact angle measurements were prepared by placing a few drops of DBTO/methanol solution on one side of a horizontal film, allowing them to dry, and irradiating from the opposite side (i.e., through the film) for 40 min.

Esterification. A surface-modified film was placed in 4 mL of pyridine and 66.5 mg (0.35 mmol) of 2-naphthoyl chloride. The mixture was stirred in a dry atmosphere at room temperature for 3 days and then cleaned as indicated above to remove noncovalently attached naphthyl species.

Fluorescence Quenching Studies. Each physical manipulation was performed to avoid moving the film in the fluorometer. Emission spectra (λ_{ex} = 280 nm) of esterified and NAEt-doped films were recorded in air and then in dry methanol (quartz cuvette). The methanol was removed and replaced with 3 mL of 1.0 M DMAE in methanol. Again, the emission spectra were recorded, and the fluorescence intensities at 352 nm were monitored continuously for 30−60 min.

Results and Discussion

Photochemical Processes. The photochemistry of DBTO in various liquids has been studied for more than 25 years.[21−24] Most recently, Jenks and co-workers have performed several extensive mechanistic investigations of the processes involved.[25] Irradiation of a DBTO molecule leads to efficient dissociation of the S−O bond, producing DBT and a ground-state oxygen atom (^3O_P) that is able to oxidize a wide range of solvents. In paraffinic media, hydroxylation is the major reaction mode, although dehydrogenation has been observed also. Alkenes undergo more epoxidation than hydroxylation, and benzene is oxidized primarily to phenol.[25] Hydroxylation is a stepwise process: hydrogen atom abstraction by oxygen is followed by recombination of the hydroxy and substrate radicals.[25]

Low-density polyethylene is not a homogeneous medium. It consists of crystalline domains and amorphous and interfacial regions.[26] Dopant molecules such as DBTO are able to enter only the amorphous regions and the interfacial spaces between crystalline and amorphous regions.[27,28] Even within the amorphous and interfacial regions, dopant molecules are not evenly distributed. For that reason, concentrations of dopants in a film must be considered only as an indicator of the bulk loading and are expressed per kilogram of *amorphous* (including *interfacial*) PE rather than per kilogram of amorphous and crytalline PE.

Although they contain small concentrations of double bonds,[29] the overall functionality of polyolefinic films is like that of alkanes. For this reason, we anticipated that photocleavage of DBTO in polyethylene might lead to oxidative processes such as those in liquid alkanes. However, the microheterogeneity and structural details of polyethylene can affect the quantum and chemical yields of hydroxylation by DBTO. For instance, very low concentrations of hydroxy groups are present even in the native, unmodified NDLDPE and BLDPE films (vide infra). They may have been introduced during the polymerization process,[30] during heating to make the films,[31] or during storage of the films.[32] Further oxidation of the hydroxy groups to carbonyl functionalities may occur preferentially for H atom abstractions from paraffinic environments if, as is probable, DBTO molecules seek sites within the amorphous part of greater polarity.

Interior Hydroxylation and Esterification Procedures. The procedure developed for *interior* modification of polyethylene films is illustrated in Scheme 1. First, DBTO was doped into amorphous and interfacial regions of a film using chloroform as a swelling agent.[20] Then the film was air-dried and rinsed with the nonswelling solvent methanol[20] to remove DBTO from surface-accessible sites. Chloroform was chosen as the doping solvent instead of the better swelling solvent cyclohexane[20] because DBTO is more soluble in the former.

The concentrations of DBTO in the films could be controlled by varying the initial concentration of the doping solution. Doping periods and temperature were chosen to ensure that partitioning equilibrium was established between a film and the chloroform solution. Equilibrium can be accelerated significantly by warming the mixture to slightly above ambient temperature. For instance, ca. 18 mmol/kg DBTO concentrations could be achieved in NDLDPE films doped with a large volume excess of 0.4 M DBTO/chloroform for 24 h at 40 °C, but only ca. 3 mmol/kg DBTO concentrations could be achieved at room temperature under otherwise the same conditions. A slightly less concentrated doping solution was used for BLDPE; a ca. 15 mmol/kg DBTO concentration was reached after 24 h at 40 °C.

The DBTO dopant molecules were then converted photochemically to DBT and ^3O_p atoms,[25] leading primarily to formation of hydroxy and epoxy groups along polyethylene chains that are in the vicinity of the original dopant sites. Oxygen atoms are known to abstract hydrogens from cyclohexane with a rate constant $3.4 \times 10^8\ M^{-1}\ s^{-1}$ at room temperature;[33] there is little opportunity for an ^3O_p atom to diffuse from the DBTO molecule from which it is made. Figure 1b shows the UV absorption spectra of native and DBTO-doped (interior) NDLDPE films before and after their irradiation. Comparison of these with the absorption spectrum of DBT (Figure 1a) indicates that the expected loss of oxygen from DBTO has taken place upon irradiation. DBT was confirmed as the dominant photoproduct by HPLC analyses (see Experimental Section). The absorption spectra after irradiation of DBTO on the *surface* and *interior* of BLDPE and the *surface* of NDLDPE (not shown) are like those in Figure 1a also.

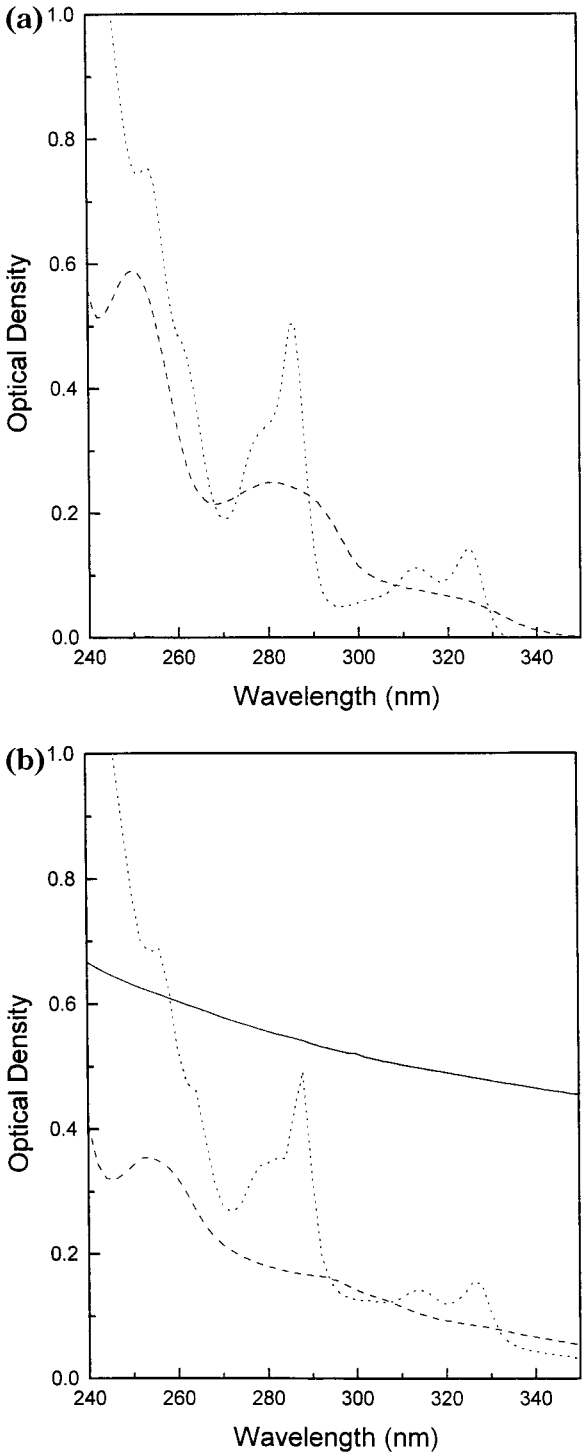

Figure 1. (a) UV absorption spectra of DBTO (- - -; 35 μM) and DBT (···; 36 μM) in hexanes and of (b) a native, undoped NDLDPE film (—), an NDLDPE film doped (interior) with ca. 2.8 mmol/kg DBTO before (- - -) and after (···) irradiation for 25 min (doping procedure: 0.08 M DBTO/$CHCl_3$ solution, 40 °C, 24 h.)

After removal of the remaining DBTO and DBT, attempts to detect the resultant hydroxy and epoxy

absorptions in the films by FT-IR spectroscopy were unsuccessful. Characteristic IR bands of DBTO were discernible before irradiation.

Films were treated with 2-naphthoyl chloride in chloroform to attach naphthyl chromophores covalently via ester linkages to *interior* (and any surface) hydroxy groups. The progress and extent of esterifications were followed by UV absorption and fluorescence spectroscopies. After exhaustive washings and extractions to remove any unreacted acid chloride, the esterified films had absorption, emission, and excitation spectra characteristic of naphthyl esters (vide infra). Esterification of *interior*-modified films proceeded well at 40 °C but not at room temperature under otherwise identical reaction conditions. We assume that the higher temperature allows molecules of 2-naphthoyl chloride to diffuse more rapidly to sites where the hydroxy groups are located and then react more easily. A similar acceleration of doping by DBTO at slightly raised temperatures was noted above.

Extensive washing by and immersion in chloroform did not remove the UV absorption or emission of naphthyl groups from the interior modified/esterified films. However, when the same procedures were applied to an NDLDPE film doped with NAEt, the naphthyl emission was lost completely. 2-Naphthoic acid, a possible noncovalently attached species, is not present in the films. It is soluble in chloroform, and its absorption and emission spectra in polyethylene are red-shifted by several nanometers with respect to those recorded for the modified/esterified films. Furthermore, an interior modified/esterified film has been immersed in water for >100 days without discernible loss of naphthyl groups. This body of data constitutes overwhelming evidence that our procedures lead to the steps outlined in Scheme 1.

Attempted Surface Hydroxylation Procedure. The DBTO deposition procedure—dipping a film into a methanolic solution for a short period and drying it horizontally in the air—ensures that dopant molecules do not enter interior regions. However, it is not clear how the heterogeneous nature of the PE film surfaces affects the distribution of DBTO molecules. We expect that they are *not* evenly distributed on a surface (as in the interior).

Attenuated total reflectance IR spectra of *surface*-modified (i.e., DBTO irradiated) NDLDPE films showed weak bands at 1724 (C═O) and 1217 (C−O) cm^{-1} that were not present in the native, unmodified films. However, no bands at >3000 cm^{-1} (indicative of O−H stretches) were evident for either the modified or unmodified films. As mentioned above, the carbonyl functionalities may arise from further oxidation of hydroxy groups by nearby DBTO molecules.

Contact angles of water droplets were measured on the surfaces of both native NDLDPE and BLDPE films and those irradiated with DBTO on one *surface*. Consistent with the paucity of hydroxy groups introduced by irradiation of DBTO on the surfaces, no apparent difference was observed between the contact angles of the modified and native films. For instance, the angles were 102.6 ± 1.1° and 99.5 ± 1.5° for native and modified BLDPE films, respectively. Similar values were found for NDLDPE films. By comparison, the contact angle of water on a low-density polyethylene film, 98.6 ± 2.5°, decreased to 60 ± 2.5° after surface treatment with chromic acid.[10b]

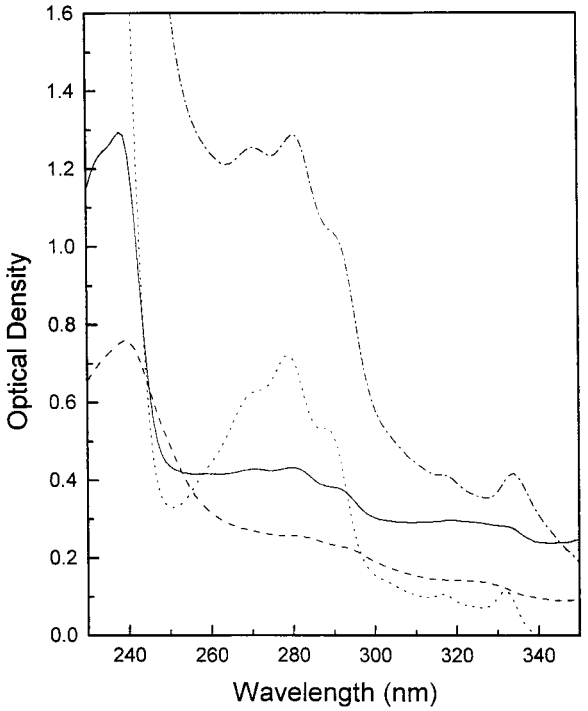

Figure 2. UV absorption spectra of NAEt in an NDLDPE film (—; ca. 5 mmol/kg) and in hexanes (···; 82 μM), an interior modified/esterified NDLDPE film (- - -; [naphthoate] ≈ 3 mmol/kg), and an interior modified/esterified BLDPE film (-·-; [naphthoate] ≈ 17 mmol/kg).

Clearly, very small area concentrations of hydroxy (and other polar) groups are introduced by irradiation of surface-deposited DBTO molecules. Our UV−vis and fluorescence measurements (vide infra) are consistent with this conclusion. We suspect that a combination of poor contact between excited DBTO molecules and film surfaces and high mobility of ^3O_p atoms at a film/air interface is responsible for the inefficiency of the surface modification.

Characterization of Modified and Esterified Films by Absorption Measurements. UV−vis absorption spectra of interior- or surface-esterified and NAEt-doped NDLDPE films and interior- or surface-esterified BLDPE films are very similar to those of NAEt in hexanes. Representative spectra are shown in Figure 2. Clearly, 2-naphthoate constitutes the vast majority of bound chromophores in the modified/esterified films.

Naphthyl groups are not attached with equal efficiencies to the two polyethylenes. Comparison of DBTO consumption and naphthyl group attachment in NDLDPE indicates that a large portion of the interior-generated ^3O_p atoms do not lead to hydroxy groups and/or some of the hydroxy groups are not esterified during the subsequent treatment with 2-naphthoyl chloride. The concentration of covalently attached naphthoate groups in NDLDPE that was *interior*-hydroxylated (by irradiation of ca. 18 mmol/kg DBTO at 400 W for 40 min) and esterified at 40 °C was estimated to be 4.7 mmol/kg by UV−vis absorption spectroscopy (Table 1). The overall efficiency of esterification is much higher in BLDPE; a film doped with ca. 15 mmol/kg DBTO, irradiated, and esterified under the conditions above was calculated to contain ca. 17 mmol/kg of covalently attached naphthyl groups (Table 2).

As mentioned previously, we infer the presence of very low concentrations of hydroxy groups in the native

Table 1. Fluorescence Quenching of Esterified NDLDPE Films by DMAE in Air at Ambient Temperature (λ_{ex} = 280 nm, λ_{em} = 352 nm)

DBTO doping[a]	*hν* time (min)	esterification procedure[b]	naphthoate concn[b] (mmol/kg)	I_{DMAE}/I_{MeOH}[c] (%)
none	0	surface	1.3	85
none	40	surface	0.6	100
surface	20	surface	0.9	92
none	40	interior + surface	0.7	72
1 interior	30	interior + surface	3.0	77
2 interior	30	interior + surface	3.7	93
3 interior	40	interior + surface	4.7	100

[a] DBTO concentrations for interior doped films are ca. 18 mmol/kg. [b] See Experimental Section for details. Surface esterifications at room temperature; interior + surface esterifications at 40 °C. [c] I_{MeOH} and I_{DMAE} are the fluorescence intensities of a film immersed in MeOH and in 1.0 M DMAE/MeOH, respectively, and recorded in that order. Care was taken not to move films between measurements.

Table 2. Fluorescence Quenching of Esterified BLDPE Films by DMAE in Air at Ambient Temperature (λ_{ex} = 280 nm, λ_{em} = 352 nm)

DBTO doping[a]	*hν* time (min)	esterification procedure[b]	naphthoate concn[b] (mmol/kg)	I_{DMAE}/I_{MeOH}[c] (%)
none	0	surface	1.3	89
none	40	interior + surface	2.8	81
interior	40	interior + surface	17	74

[a] DBTO concentrations for interior doped films are ca. 15 mmol/kg. [b] See Experimental Section for details. Surface esterifications at room temperature; interior + surface esterifications at 40 °C. [c] I_{MeOH} and I_{DMAE} are the fluorescence intensities of a film immersed in MeOH and in 1.0 M DMAE/MeOH, respectively, and recorded in that order. Care was taken not to move films between measurements.

polyethylene films, although they are not detectable by IR spectroscopy. The basis for this assertion lies in our ability to attach low concentrations of 2-naphthoyl groups to native films by the same esterification procedures for the modified films. The concentrations of 2-naphthoate groups introduced into NDLDPE that had been irradiated in the absence of DBTO were actually somewhat *less* than those achieved with the native films (Table 1); just the opposite result is obtained from BLDPE films (Table 2).

We suggest that the large disparity between the results with the two films is related to their morphological and structural differences. BLDPE has a larger amorphous region and fewer unsaturated groups than NDLDPE.[15] The morphology of BLDPE facilitates the entry of dopant molecules into its interior regions, and its lower concentration of double bonds may favor formation of hydroxy groups from ^3O_P atoms. Thus, more hydroxy groups should be produced in BLDPE than in NDLDPE when the initial concentrations of DBTO are about the same and the films are irradiated under the same conditions. In addition, we have noted that the morphology of even one type of polyethylene varies somewhat from piece to piece; note that even the two modified/esterified NDLDPE films in Table 1 that were prepared in the same way are quenched to somewhat different extents by DMAE. Morphology and structure do make a difference in PE films, but so do stochastic measurements.

Characterization of Modified and Esterified Films by Emission Measurements. The excitation and fluorescence spectra presented in Figures 3−5 also

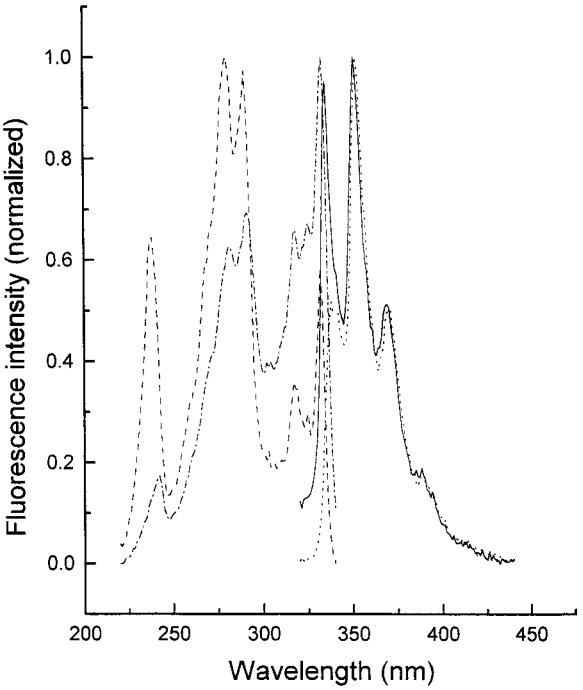

Figure 3. Excitation (- - -, -··-) and emission (—, ···) spectra of NAEt in cyclohexane (0.3 mM) and in an NDLDPE film (ca. 5 mmol/kg) in air. λ_{ex} = 280 nm, λ_{em} = 352 nm.

indicate that naphthoate groups constitute the vast majority of the emitting species in the films. The minor differences in the 310−350 nm region of the excitation spectra of Figure 4a suggest the presence of a small amount of a second species whose possible origin and nature are discussed later.

DMAE is an efficient quencher of excited singlet states of aromatic molecules. More than 95% of the fluorescence intensity from 1.1×10^{-4} M NAEt in methanol is quenched by 1.0 M DMAE. However, the quencher molecules do not penetrate beyond the surfaces of PE films[12a,34] when dissolved in a nonswelling methanol solution.[20] Thus, the fraction of naphthyl chromophores attached at or near the surfaces can be approximated from the fluorescence intensities of a film in methanol and in 1 M DMAE/methanol.

Quenching results for films esterified according to various protocols are presented in Tables 1 and 2. The fluorescence intensities are virtually constant for many minutes after films are placed in a methanolic solution of the quencher. However, there appears to be a very slow hydrolysis or cross-esterification process that leads to loss of surface-attached groups.

Only a small portion of the fluorescence intensity from *surface*-esterified native films or films irradiated in the absence of DBTO and then esterified is quenched by methanolic DMAE. These results indicate that most of the hydroxy groups present in native films are remote from the surfaces. *Interior* modified/esterified films also retain a significant fraction of their fluorescence in the presence of DMAE. Although differences in film morphology and structure mentioned above may explain why quenching of naphthoate fluorescence from interior modified/esterified BLDPE (ca. 25%; Table 2) is more efficient than from the corresponding NDLDPE films (10% av; Table 1), other related factors, such as permeability of DMEA in the two polymers, may also contribute.

Temporal fluorescence decay profiles of the films were obtained by the time-correlated single photon counting

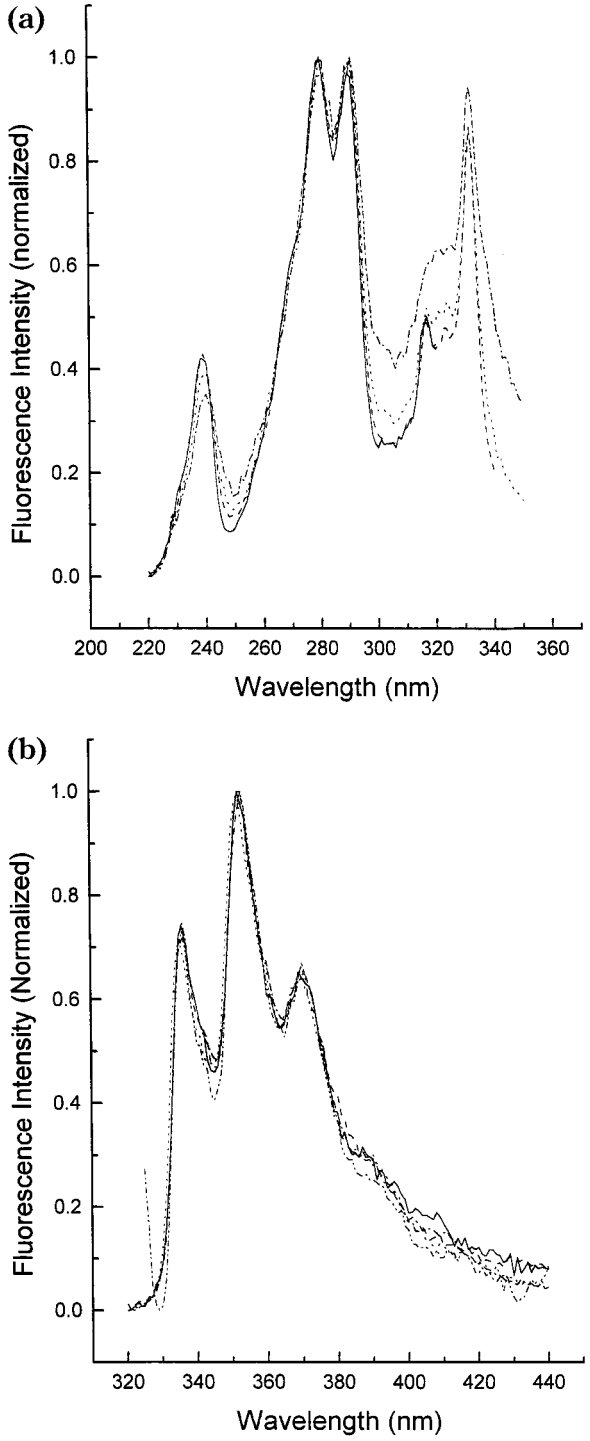

Figure 4. Excitation (a) and emission (b) spectra of an interior modified/esterified NDLDPE film ([naphthoate] ≈ 3 mmol/kg) in air. For (a), λ_{em} = 336 (−), 352 (- - -), 370 (···), and 388 nm (-·-). For (b), λ_{ex} = 239 (−), 271 (- - -), 280 (···), 291 (-·-), and 317 nm (-··).

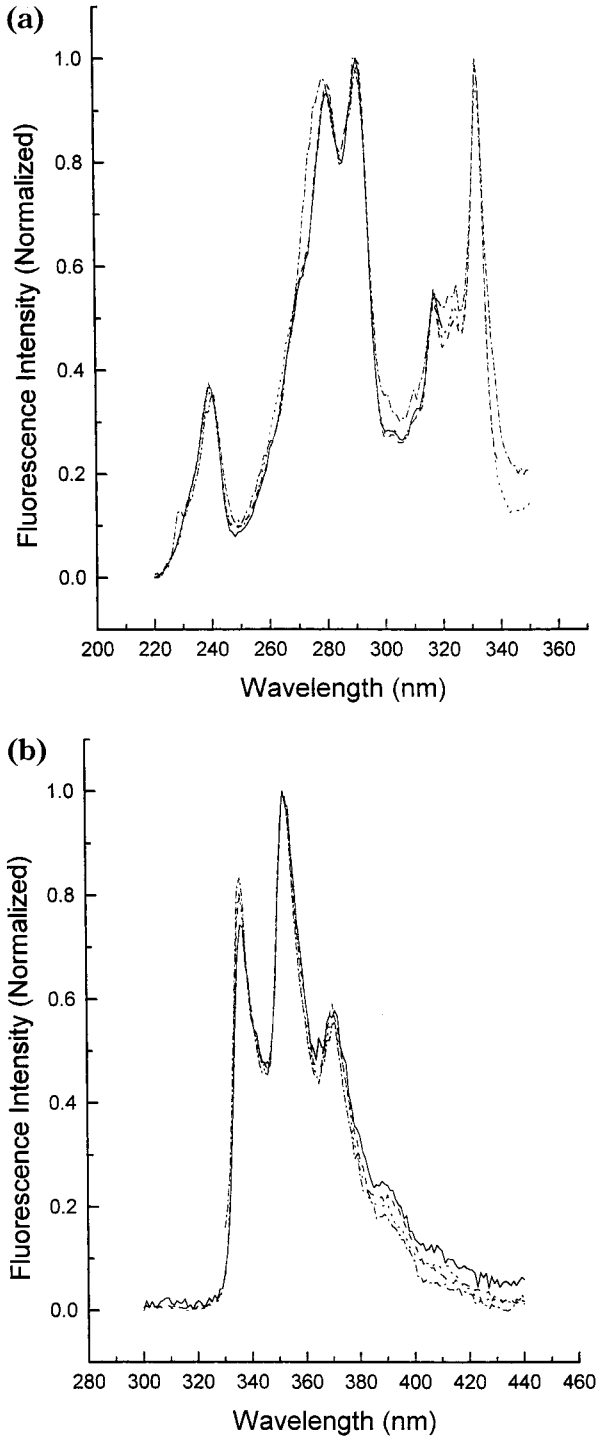

Figure 5. Excitation (a) and emission (b) spectra of a surface modified/esterified NDLDPE film ([naphthoate] ≈ 0.9 mmol/kg) in air. For (a), λ_{em} = 336 (−), 352 (- - -), 370 (···), and 388 nm (-·-). For (b), λ_{ex} 239 (−), 280 (- - -), 290 (···), and 317 nm (-·-).

(TCSPC) technique. Results from a native NDLDPE film doped with NAEt are presented in Table 3. A component from light scatter from film surfaces is not reported. The dominant decay constant, τ_1 = 14.3 ns (in air), is very close to the literature value for NAEt in degassed cyclohexane, 14.9 ns.[35] A small amount of a shorter-lived decay component ($\tau_2 \approx$ 3.4−5.7 ns) was detected, also at λ_{ex} = 290 nm (i.e., the red edge of absorption where excitation of minor emitting species can become more prominent). There is essentially only one decay component from NAEt in NDLDPE. This conclusion is also supported by a global analysis of the data: $\tau_1 = 14.3 \pm 0.1$ ns (A_1 = 1.0) and global χ^2 = 1.170.

Two comparable decay components (in addition to that from scatter) were detected from an interior modified/esterified NDLDPE film (Table 4). The one with the longer decay constant, τ_1, is assigned to the fluorescence from naphthoate groups covalently attached to polyethylene chains. By global analysis of the decays, $\tau_1 = 14.3 \pm 0.9$ ns (A_1 = 0.70), $\tau_2 = 8.8 \pm 1.4$ ns (A_2 = 0.30), and global χ^2 = 1.260. The ratios of the preexponential terms and the magnitudes of τ_1 and τ_2 in air and when the

Table 3. Decay Constants (τ_i)[a] and Relative Preexponential Factors (A_i)[b] for an NDLDPE Film Doped (Interior) with ca. 5 mmol/kg NAEt at Room Temperature in Air (Data Associated with Scatter ($\tau \approx 1$ ns) Are Not Included)

λ_{ex} (nm)	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	A_1	A_2	χ^2
280	336	14.3 ± 0.0		1.0		1.017
	352	14.2 ± 0.1		1.0		1.163
290	336	14.4 ± 0.0	3.4 ± 0.6	0.95	0.05	1.029
	352	14.5 ± 0.0	5.7 ± 0.9	0.94	0.06	1.083

[a] Error limits are one standard deviation. [b] A_i values are normalized.

Table 4. Decay Constants (τ_i)[a] and Relative Preexponential Factors (A_i)[b] for an Interior Modified and Esterified NDLDPE Film (ca. 3.0 mmol/kg) at Room Temperature in Air (Data Associated with Scatter ($\tau \approx 1$ ns) Are Not Included)

λ_{ex} (nm)	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	A_1	A_2	χ^2
280	336	13.6 ± 0.1	4.5 ± 0.3	0.76	0.24	1.109
	352	14.2 ± 0.4	8.4 ± 1.1	0.71	0.29	1.022
290	336	14.3 ± 0.1	4.8 ± 0.1	0.48	0.52	1.202
	352	14.3 ± 0.1	4.9 ± 0.1	0.46	0.54	1.175
	370	14.2 ± 0.1	5.4 ± 0.3	0.54	0.46	1.225

[a] Error limits are one standard deviation. [b] A_i values are normalized.

Table 5. Decay Constants (τ_i)[a] and Relative Preexponential Factors (A_i)[b] for an Interior Modified and Esterified BLDPE Film (ca. 17 mmol/kg) at Room Temperature in Air (Data Associated with Scatter ($\tau \approx 1$ ns) Are Not Included)

λ_{ex} (nm)	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	A_1	A_2	χ^2
280	352	13.2 ± 0.1	6.4 ± 0.2	0.77	0.23	1.152
290	352	13.3 ± 0.1	6.7 ± 0.6	0.75	0.25	1.159

[a] Error limits are one standard deviation. [b] A_i values are normalized.

film was immersed in 1.0 M DMAE/methanol were very similar. Thus, although the nature of the τ_2 component is unknown, it does not derive from naphthoate groups attached to film surfaces. It is intrinsic to NDLDPE, since it is the dominant emitting species in native NDLDPE films and in an interior-modified (but not esterified) one. Its low concentration and absorbance did not allow detection by UV−vis absorption or steady-state fluorescence. The fact that the magnitude of neither of the two decay constants is lowered in the quenching solution suggests that both emitting species are located primarily at interior sites of the film. The same two decay components were also detected in NDLDPE films that had been irradiated with or without DBTO and then esterified on the surfaces.

An interior-modified and esterified BLDPE film showed two decay components also. At $\lambda_{ex} = 280$ and 290 nm and $\lambda_{em} = 352$ nm, the average τ_1 is 13.2 ± 0.1 ns ($A_1 = 0.76$) and τ_2 is 6.5 ± 0.6 ns ($A_2 = 0.24$) (Table 5). The τ_2 component is again due to a lumophoric group intrinsic to the film. The decay constant ascribed to naphthyl fluorescence, $\tau_1 = 13.2$ ns, is slightly smaller than that in NDLDPE. We consider this small difference mechanistically unimportant, since the two film types are not the same morphologically or structurally.

Conclusions

We have demonstrated that photolysis of DBTO in the amorphous (interior) portions of polyolefinic films leads to reasonably efficient and selective hydroxylation of polymer chains. Most importantly, hydroxylation of film surfaces can be minimized. In fact, attempts to hydroxylate surfaces selectively using similar irradiation techniques were not successful. Esterification by treatment of interior modified films with an acid chloride (2-naphthoyl chloride in this work) introduces chromophoric/lumophoric groups that are highly resistant to removal by moisture.

Although many methods for surface modification of polyolefinic materials are available, there are few that are selective for interior modifications. The one described here appears to be quite diverse in the range of groups that can be appended. In principle, any acid chloride, acid anhydride, etc. capable of esterifying an alcohol should be attachable to interior sites of polyolefinic materials using the protocols described. Furthermore, we have irradiated DBTO-doped films through a mask and then esterified them with 2-naphthoyl chloride to imprint a permanent, robust image that can be read most easily with a fluorescent “black light”.

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