PHOTOCHEMICAL AND PHOTOPHYSICAL APPROACHES TO THE CHARACTERIZATION OF THE SHAPES, FREE VOLUMES AND ACCESSIBILITIES OF GUEST SITES IN LOW-DENSITY POLYETHYLENE FILMS†

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Various luminescence and photochemical techniques have been developed to probe the natures of the sites available to guest molecules in low-density polyethylene films. The methods, which include covalent modification of interior sites with fluorophores, are described. The results indicate that a distribution of site types, each with its characteristic shape, free-volume, and accessibility, are present. Furthermore, this distribution is changed drastically when a film is stretched.

Keywords: photochemistry; low-density polyethylene films.

INTRODUCTION

A naive description of polyethylene is that it is a solid aggregate of long normal paraffin molecules. In fact, the rubric "polyethylene" is used to identify literally thousands of polymer formulations, derived in some cases from mixtures of monomers which include 1-alkenes in addition to ethylene. Molecular weight average and distribution, degree of chain branching, mode of processing, degree of crystallinity, types of amorphous regions, density etc. differentiate the various polyethylenes.

Two general site types in low-density polyethylene (LDPE) -near points of chain-branching and along the interfaces between amorphous and crystalline regions - have been suggested for guest (dopant) molecules.[1] Guest molecules are unable to enter the crystalline portions of LDPE.[2]

To characterize further the microscopic environments provided by LDPE to guest molecules, we have probed the shapes and free volumes of the sites and the dynamics of diffusion to and from them in several different ways. The results obtained thus far indicate that there is a distribution of site types which can be changed drastically by macroscopic stretching of polymer sheets. The complexity of the behavior of the probe molecules in LDPE demonstrates that the analogy with an exceedingly long paraffin is incorrect and very misleading. A review of our efforts to clarify the structural and dynamic properties of guest sites in LDPE is presented.[3]

MATERIALS AND PROCEDURES

Films of Sclairfilm (76 mμ thick, 0.92 g/cc3, Mw 112600, from DuPont of Canada), a low-density polyethylene (LDPE), have been employed throughout our investigations. This allows results from different experiments to be compared directly. The films were soaked in chloroform before being used in order to remove plasticizers, antioxidants, and other additives. Reagents, solvents, and methods are as described in our cited publications.

Cold-stretching to 4-6X the original film length was accomplished with a device designed for this purpose or by hand; experiments employing the two methods led to indistinguishable results.

SPECTROSCOPIC INVESTIGATIONS

Michl and Thulstrup,[4] especially, have shown that doped, stretched films of LDPE can be used to align guest molecules according to a laboratory frame of axes. Linear dichroic spectra of the dopant molecules provides information concerning the transition dipole of the electronic transitions.

Since it has been conjectured that dopant molecules translocate from one site type to another when LDPE films are stretched,[2,5] we sought to devise an experiment in which the dopant molecules are forced to remain at their original location, regardless of the applied stress on the material. To accomplish this goal, (9-anthryl)methyl groups, in very low concentrations (10^{-3}-10^{-4} M), were attached covalently to interior positions of films (An-LDPE).[6] Subsequently, the films were stretched. For comparison purposes, another piece of film was doped with an equal concentration of 9-methylanthracene (MA, a non-covalently attached guest) and stretched by the same amount.

Fluorescence spectra of covalently-attached films gave no evidence for excimer emission; none was expected since the concentrations of lumophores was purposely kept very low. Thus, we assume that virtually all of the occupied sites have no more than one anthryl group in each. Similarly, no excimer emission could be detected from LDPE films with 10^{-3}-10^{-4} M 1-pyrenyl groups appended covalently to polymer chains at internal sites (Py-LDPE).[7] Much higher concentrations of non-covalently linked pyrene in the films did provide emission spectra with detectable excimer emission (Figure 1).

The emission anisotropy of an unstretched An-LDPE film is ca. 0.15-0.18,[6a] indicating that the anthryl groups are not able to move rapidly within a film. When swelled by ca. 17% by cyclohexane, the films become more tolerant of anthryl motions and the emission anisotropy decreased to ca. one-third of its original value.[6a]

Unstretched An-LDPE films and MA/LDPE films showed no linear dichroism (d): $d = OD_{\parallel}/OD_{\perp}$ was unity at 260 and 390 nm, wavelengths at which anthryl transition dipoles are polarized almost exclusively along the long (Z) and short (Y)

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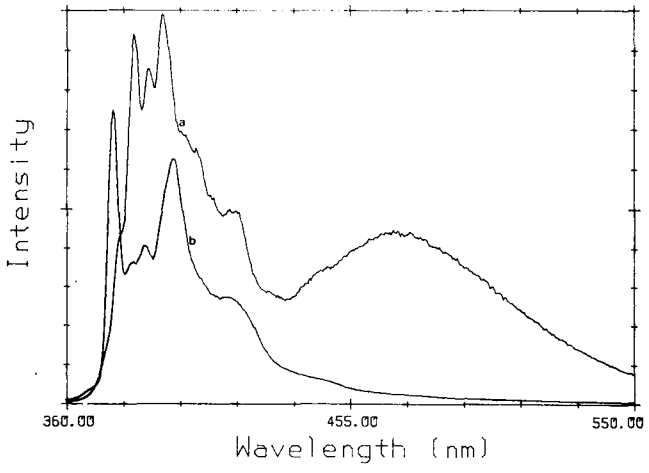


Figure 1. Room temperature emission spectra in air (a) from an LDPE film after immersion in a 0.24 M pyrene in chloroform solution for ca. 12 h (Py/LDPE) and (b) from a film, doped as above, after being irradiated for 1 h and exhaustively extracted with chloroform (Py-LDPE). The spectra are not normalized; λ_{ex} 343 nm.[7]

in-plane axes. However, the same films, after being stretched to 5 X their original lengths, displayed non-unity dichroic ratios from which orientation factors ($O_f = d_f/[d_f + 2]$ where f = X,Y,Z are the principal axes of anthracene) can be calculated.

As shown in Table 1, the values calculated by us for MA differ somewhat from those reported by Michl and Thulstrup.[8] The disparities can be attributed to different degrees of stretching, different LDPE sources, and different concentrations of MA the two experiments. More importantly, an internal comparison between our results from An-LDPE and MA/LDPE, with about equal chromophore concentrations, reveals that the in non-covalently and covalently attached anthryl groups reside in nonequivalent site types after film stretching. Although these results do not confirm the hypothesis that guest molecules translocate when films are stretched,[5] they are at least consistent with it.

Table 1. Dichroic ratios and orientation factors from anthryl groups in stretched LDPE films.[6]

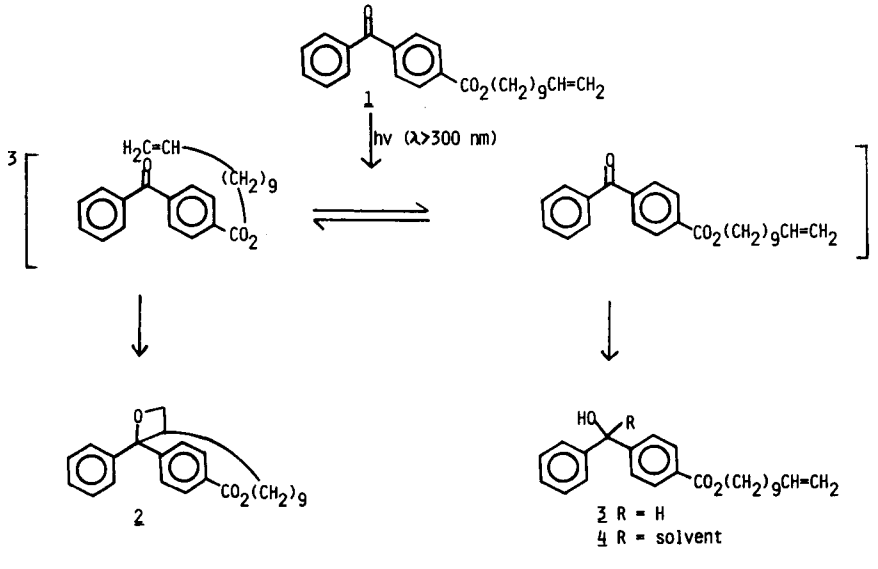
dopant	d_X	d_Z	O_X[b]	O_Y	O_Z
MA	0.77	2.8	0.14	0.28	0.58
MA[a]			0.20	0.29	0.51
An-LDPE	0.89	1.94	0.21	0.30	0.49

a) Data from Michl and Thulstrup.[8] b) Calculated assuming $O_X = 1 - (O_Y + O_Z)$.[4]

REACTIONS OF GUEST MOLECULES

There have been few reports of reactions of guest molecules in LDPE films and still fewer ones in stretched LDPE films.[9] In addition to the previously mentioned derivatizations of LDPE at interior sites with 1-pyrenyl and (9-anthryl)methyl groups, we have explored the influence of unstretched and stretched LDPE films on the ability of conformationally labile guest molecules to undergo specific transformations. Comparisons between results from those experiments in unstretched and stretched films and between films and normal isotropic solvents have been useful in establishing the qualitative nature of the dopant sites.

Thus, the excited triplet state of 10-undecenyl benzophenone-4-carboxylate (1) is known to yield (intermolecular) photoreduction (3 or 4) and (intramolecular) Paterno-Buchi cyclization (2) products (Scheme 1).[10] The ratio between them depends upon the proximity of the ϖ-vinyl and carbonyl groups at the moment of excitation and their ability to approach each other during the triplet lifetime of 1. When access to the vinyl group by the carbonyl is hindered by the local environment, more 3 and 4 is predicted; when the vinyl and carboxyl are forced to be near each other, 2 should be formed preferentially. Using this simple hypothesis, the fate of irradiated 1 in n-hexane and in unstretched and stretched LDPE films was determined. As expected, the yield of reduction photoproducts is more than twenty times greater than that of 2 in hexane.[11] Constraining the undecenyl chain of 1 within the volume allocated by sites of unstretched LDPE increases the relative yield of cyclization products by ca. four-fold. Stretching the films results in a further increase in the relative yield of 2, reducing the ratio of 3/2 to less than 3.[11]



Scheme 1. Photochemical reactions of 10-undecenyl benzophenone-4-carboxylate (1) in hydrocarbon media.[11]

Since the relative yields of photoproducts did not change with the extent of conversion of 1, there must be only one site type available to it in unstretched and stretched LDPE, the quantum yields for conversion of 1 in each of several site types must be about equal, or the rate of hopping among sites must be more rapid than the rate at which photoproducts form. Regardless of which scenario is correct, the average site environment must be one in which the undecenyl chain spends a large fraction of time draped over the benzoyl portion of the molecule. Stretching serves only to increase this fraction further rather than to allow the molecule to adopt more extended (rod-like) conformations. Thus, the shape of sites in unstretched LDPE seems to be more cylindrical than thin and rod-like. Macroscopic stretching of a film appears to reduce the free volume of an occupied site without changing appreciably its shape.

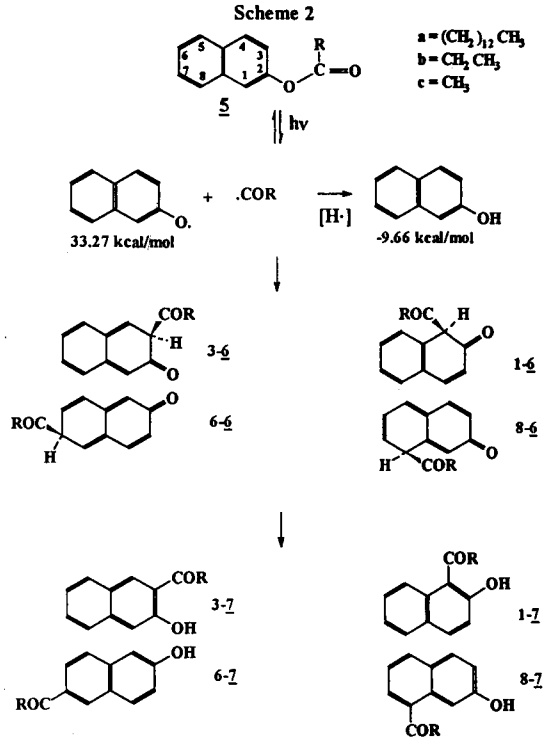
Further insights into the shapes and volumes of LDPE dopant sites is provided by an investigation of the photo-Fries rearrangement[12,13] of 2-naphthyl myristate 5a.[14] Through attempted triplet sensitization experiments, we have ascertained that the likely reactive excited state is the singlet.[14]

The mechanism appears to involve homolytic cleavage of the acyl-oxy bond, producing a spin-correlated pair of radicals which either react intramolecularly or diffuse apart and abstract a hydrogen atom from solvent.[12] The consequences of these events are shown in Scheme 2. In addition to reformation of 5a, the radical pair may also recombine to yield any of four keto-isomers (6). These are the recombination products predicted to be feasible on the bases of simple valence-bond arguments, calculated heats of formation (thermodynamic stability), and odd-electron densities on the 2-naphthyloxy radical (kinetics arguments) (Table 2).[14] Enolization of 6 yields the isolated isomers 7.

Table 2. Heats of formation of possible intermediates 6 from a model compound, 2-naphthyl propanoate (5c), and spin density at various carbon atoms of the 2-naphthoxy radical as calculated by the MNDO method.[14]

position or isomer	ΔH_f of 6c (kcal/mol)	2-naphthoxy spin density
1	-34.2	0.40
3	-21.5	0.06
4	20.1	0.01
5	22.2	0.00
6	-19.4	0.13
7	22.2	0.00
8	-18.2	0.10

Scheme 2



Scheme 2. Mechanistic scheme for the photo-Fries rearrangements of 2-naphthyl acylates (5), showing potential intermediates and products. The heats of formation for the 2-naphthyloxy radical and 2-naphthol are calculated by the MNDO technique.[14]

The distribution of photoproducts from 5a was investigated initially in a series of low molecular weight solvents (Table 3). The results indicate that traces of moisture have a marked effect on the course of reaction. The absence of 2-naphthol from irradiation of 5a in moist hexane and its dominance in anhydrous hexane seems, at first glance, incongruous. If anhydrous n-hexane were free of impurities (which can act as good H-atom donors), very little 2-naphthol should form since abstraction from hexane by 2-naphthol is endothermic: our MNDO calculations predict that 2-naphthyloxy radicals can abstract H-atoms from bonds no stronger than ca. 43 kcal/mol. A possible explanation for the lack of 2-naphthol in moist hexane is that the potential H-atom donor impurities are polar and aggregate in aqueous microdroplets which are difficult to access by 2-naphthyloxy radicals. Alternatively, the water molecules may stabilize 2-naphthyloxy radicals or keep the initial radical pair in contact for a longer period of time. Subsequent experiments in protic solvents favor the latter explanation, although the evidence in hand is insufficient to dismiss either one.

Table 3. Photoproduct distributions from irradiation (>300 nm) of 5a in various solvents and LDPE films under nitrogen.[14]

				relative yields			
[5a],M	medium	T(°C)	% conversion	2-naphthol	1-7	3-7	6-7
6.2×10^{-4}	hexane (dry)	50	14	85	14	0	1
6.2×10^{-4}	hexane (moist)	50	8	trace	95	0	5
(1 wt %)	heneicosane (C21H44)	50	12	38	53	0	9
(1 wt %)	n-butyl stearate	32	8	68	22	0	10
6.8×10^{-4}	ethanol	25	12	26	63	0	10
4.9×10^{-3}	t-butyl alcohol	25	12	trace	86	0	14
LDPE							
5x10-4-10^{-3}	unstretched	25	≤7	0	0	75	25
5x10-4-10^{-3}	stretched	25	≤7	0	0	92	8

Isotropic heneicosane's higher viscosity may hold the initially formed radical pair together for a longer period, increasing the probability of 6 isomers being formed. When viscous solvents are comprised of molecules with more easily abstractable H-atoms, like n-butyl stearate, formation of 2-naphthol is able to compete more efficiently with radical recombination pathways. In lower-viscosity polar solvents with easily abstractable H-atoms, like ethanol, the apparent stabilization of the 2-naphthyloxy radicals by hydrogen bonding partially counterbalances the propensity to form 2-naphthol. The influence of hydrogen bonding on the course of reaction is demonstrated further in t-butyl alcohol, a solvent which does not have easily abstractable H-atoms and which results in only trace amounts of 2-naphthol.

Equally noteworthy is the fact that in all of the solvents, only two of the "favored" 7 isomers are detected, and 1-7 is always preferred over 6-7. Although the dominance of 1-7 is expected from the data in Table 2, the absence of 3-7 and 8-7 is not.

With these data as benchmarks for the behavior of radical pairs from 5 in fluid, isotropic media, their fate in LDPE films was examined. Irradiations to various conversions produced virtually identical photoproduct ratios. In unstretched LDPE, neither 2-naphthol nor 1-7 could be detected. Instead, a 3/1 ratio of 3-7/6-7 was found. In stretched LDPE films, irradiation led to an even more pronounced preference for 3-7.

When viewed in light of the solution results, these photoproduct distributions are remarkable. They are consistent with a model for the sites afforded molecules of 5a which is very similar to that advanced to explain the results from irradiation of 1.[11] The sites must be limited in free volume and rather globular in shape. As indicated by the absence of 1-7 and the appearance of a new photoproduct, 6-7, the sites must not favor the formation of photoproducts which are both wide and long. However, the results with 1 and 5a suggest that the average shape of the occupied sites in LDPE may be more cylindrical than globular. In any case, the lack of 1-7, the preferred photoproduct in solution, requires that the long acyl radical and 2-naphthyloxy radical not be able to recombine at the 1-position (i.e., forming the more globular and less rod-like 1-6); the recombination clearly favors 6 isomers whose length to breadth ratio is high in extended conformations. Reduced selectivity in the photoproduct distribution from 2-naphthyl acetate (5c) in LDPE[14] again supports the model in which LDPE sites are more tolerant of guests with large length to breadth ratios.

Guests with large length-to-breadth ratios. The data also demonstrate that the sites afforded by LDPE can influence not only the distribution of photoproducts from guests, but also lead to the formation of new photoproducts not observed from irradiations conducted in homogeneous fluid media.

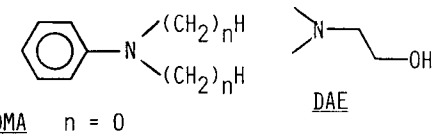
DISTRIBUTIONS OF GUEST SITE SIZES

Information presented thus far indicates that different site types may exist in LDPE, but does not address quantitatively their free volumes. Since pyrene excimer emission can be detected from LDPE films which were swollen by chloroform at the time of doping,[7] some of the sites must have a minimum of ~645 Å^3 (i.e., the sum of the van der Waals volumes of two pyrene molecules) of available free volume. However, this volume may not be representative of sites in unswelled LDPE.

In other experiments, Py-LDPE (and An-LDPE) films were placed in methanolic solutions of dialkylanilines (DAA) until the pyrenyl (or anthryl) fluorescence intensity no longer changed. Since methanol is a non-swelling solvent for LDPE, DAA molecules had to enter unswelled films and occupy sites more indicative of the native polymer. The concentrations of DAA in the films were ascertained from the film volumes and the quantity of DAA which could be extracted from them. Some of the pertinent data for Py-LDPE is presented in Table 4.[15]

F, the fraction of film fluorescence quenched by a DAA homologue, is expressed in eq. 1[7] where I_o and I_{eq} are the fluorescence intensities observed in the absence of DAA and after equilibration with it. Since DAA are known to be very efficient (diffusion controlled) quenchers of pyrenyl and anthryl excited singlet states,[16] the values of F represent the fraction of pyrenyl or anthryl occupied sites which also contain at least one DAA molecule. From the volumes of pyrenyl, anthryl, and the DAA, the distribution of the minimum free volumes at the sites containing fluorophores can be calculated.

$$F = (I_o - I_{eq})/ I_o \quad (1)$$



DAE

DMA n = 0
DEA n = 1
DPA n = 2
DBA n = 3

The values of F for one DAA homologue are larger in unstretched than in stretched films. However, the dependence of F on the molecular volume of DAA is greater for the stretched films. Since the total concentration of DAA in a film, $[DAA]_{film}$, depends upon its initial concentration in the methanolic doping solution and its partition coefficient, the values of F were normalized with respect to DAA (F_M in eq. 2). The F_M values

are more indicative of the ability of a DAA to enter a site which is already occupied by a covalently attached fluorophore and of the distribution of free-volumes at such sites.

$$FM = F/[DAA]_{film} \quad (2)$$

From the absence of change in FM using unstretched films, we conclude that the total free volume of pyrenyl-occupied sites which are quenchable by any DAA must be at least ~555 Å^3, the sum of the van der Waals volumes of pyrenyl and DBA (the largest DAA employed). Furthermore, the ac-

Table 4. Data related to fluorescence quenching in Py-LDPE films by DAA homologues at 25°C.[15]

DAA	van der Waals	unstretched film			stretched film		
	volume, Å^3	$[DAA]_{film}$,M	F	F_M,M^{-1}	$[DAA]_{film}$	F	F_M,M^{-1}
DMA	128.7	0.19	0.35	1.6	0.14	0.15	0.9
DEA	162.8	0.12	0.25	1.7	0.09	0.10	0.9
DPA	196.9	0.09	0.19	1.6	0.08	0.04	0.3
DBA	231.0	0.07	0.16	1.6	0.09	<0.02	<0.1

cess route to those sites must not have a constriction point whose diameter is smaller than that of a DAA molecule. These data presented graphically in Figure 2, demonstrate the striking difference between unstretched and stretched films. In the latter, the accessible sites can be bracketed to have average free volumes between ~485 and 519 Å^3. As judged from the large decreases in F_M between DEA and DPA or between DPA and DBA ($\Delta V \cong$ 34 Å^3), the distribution of volumes within these sites is rather narrow. Comparatively, DMA is less than twice as efficient a quencher in unstretched as in stretched Py-LDPE films, but DBA is more than 10 times more efficient in the unstretched film.

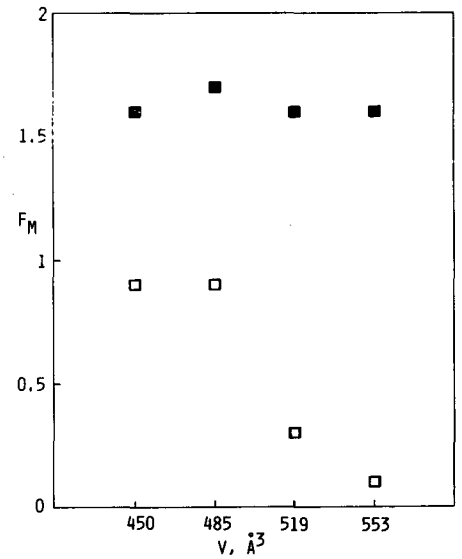


Figure 2. FM versus the sum of the calculated van der Waals volumes, V, of one pyrenyl group and one DAA molecule; from out-diffusion data using unstretched (■) and stretched (□) Py-LDPE films.[15]

Since the information on FM that this method provides is limited only to sites with covalently bound fluorophores, we also examined the influence of their concentration in An-LDPE films.[6] Thus, using DMA as the quencher, the F_M values were found to remain constant over a five-fold change of concentration of anthryl groups in unstretched films (Table 5). However, the corresponding stretched films exhibited FM values which increase as the anthryl concentration decreases. These results are totally consistent with those in Table 4. They provide additional insights, suggesting that DMA is distributed rather evenly throughout the amorphous regions of the polymer.

Table 5. Data related to fluorescence quenching of An-LDPE films by DMA at 25°C.[6]

[An],M	unstretched film[a]		stretched film[b]	
	F	F_M,M^{-1}	F	F_M,M^{-1}
7.8x10^{-4}	0.34	1.8	0.12	0.9
6.5x10^{-4}	0.34	1.8	0.15	1.1
1.6x10^{-4}	0.35	1.8	0.21	1.5

a) $[DMA]_{film}$ = 0.19M, b) $[DMA]_{film}$ = 0.14 M.

RATES OF DIFFUSION IN LDPE FILMS

As alluded to in the discussion above, an impediment to the quenching of covalently attached fluorophores in LDPE films may be imposed by restriction of polymethylene chains along the pathway followed by DAA molecules from a film surface to an occupied site.

If a Py-LDPE or An-LDPE film is placed in a DAA/methanol solution, the decreasing intensity of fluorescence from the film (by exciting at a wavelength where DAA does not absorb and by monitoring the emission at one wavelength) can be followed with time until a minimum (equilibrium) value is reached. When the DAA-doped film is then placed in methanol (or another non-swelling liquid in which DAA is soluble), the increasing intensity of fluorescence can be monitored with time. Typical intensity plots are shown in Figures 3 and 4. Provided the methanol is in extremely large excess of the film volume, virtually all of the DAA will diffuse eventually from the film and the fluorescence intensity will attain a maximum value.

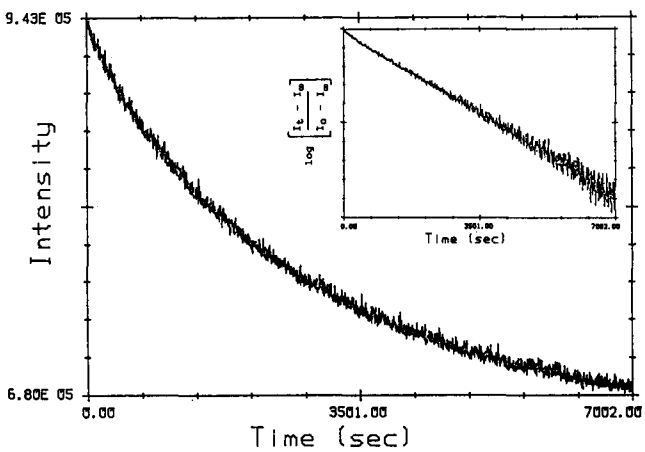


Figure 3. Fluorescence decay (in-diffusion) curve from an unstretched Py-LDPE film in contact with 0.5 M DMA and 0.1 M 2-dimethylaminoethanol (DAE, a quencher of surface pyrenyl groups) in methanol at 7•C, λ_{ex} 343 nm; λ_{em} 395 nm. The inset is a plot of the data according to eq. 3a.[7]

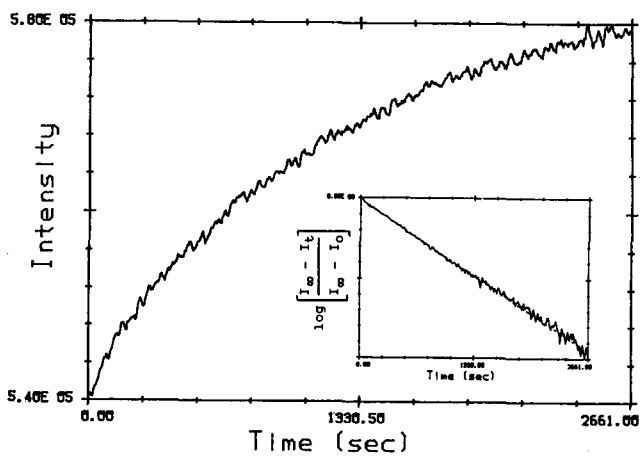


Figure 4. Fluorescence growth (out-diffusion) curve from a stretched Py-LDPE film, previously doped with DMA and in contact with methanol, at 22°C. λ_{ex} 343 nm; λ_{em} 395 nm. The inset is a plot of the data according to eq. 3b.[7]

Manipulation of this data as being due to competing first-order rate processes or being due to Fickian diffusion (second law) allows characteristic values for DAA migration from the films to be calculated. The two expressions, for the rate constant (k) and the diffusion coefficient (D), are presented in their integrated forms in equations 3 and 4, respectively. Plots of the data in Figures 3 and 4, but treated according to equations 3a and 3b, respectively, are presented as insets. A typical fluorescence decay (in-diffusion) curve using DMA and an An-LDPE film is presented in Figure 5a; the data are treated in Figures 5b and 5c according to eqs. 3a and 4a, respectively. In principle (and practice), k (or D) from in-diffusion (initial doping) or out-diffusion (from film to methanol) experiments may lead to slightly different values due to the liquids in contact with a film not being exactly the same in the two cases.[7] For the purposes of the general discussions here, this factor will be ignored. In eqs. 3a and 4a, I_∞, I_t, and I_o are the fluorescence intensities from the film after complete in-diffusion, after a time=t, and before entry by DAA into a film; in eqs. 3b and 4b, I_∞ is the fluorescence intensity after complete loss of DAA from the film and I_o is the intensity from the film in its maximally-doped state; l is the film thickness.

$$\ln[(I_o-I_t)/(I_o-I_\infty)] = -kt \quad (3a)$$

$$\ln[(I_\infty-I_t)/(I_\infty-I_o)] = -kt \quad (3b)$$

$$(I_o-I_t)/(I_o-I_\infty) = (4/l)(D/\pi)^{1/2}t^{1/2} \quad (4a)$$

$$(I_\infty-I_t)/(I_\infty-I_o) = (4/l)(D/\pi)^{1/2}t^{1/2} \quad (4b)$$

By performing experiments over a temperature range which does not include a phase change of LDPE, it is possible to calculate the activation energies, E_a and E_D, associated with k and D (equations 5 and 6). Thus, the values of Ea or E_D can be determined from the slopes of plots of ln k or ln D versus the inverse of temperature.

$$k = k_o\exp(-E_a/RT) \quad (5)$$

$$D = D_o\exp(-E_D/RT) \quad (6)$$

E_a values from fluorescence growth curves (i.e., DAA out-diffusion experiments) using one set of Py-LDPE films are collected in Table 6. They indicate that the resistance to DAA motion increases as its size decreases. Furthermore, it is more difficult to remove DAA molecules from sites in the stretched film than in the unstretched one. It should be remembered that the physical process being measured in these experiments is removal of the last (and probably only) DAA molecule from a site occupied by a pyrenyl group. Only if that process is fast with respect to motion of DAA molecules within the bulk should the activation energies in Table 6 be related to diffusion. That they are is indicated by the similarity between the Ea from fluorescence decay (in-diffusion) and fluorescence growth (out-diffusion) experiments: for DMA as quencher, the E_a from in-diffusion experiments for the films of Table 6 are 13.5±0.5 (unstretched) and 17.4±0.8 kcal/mol (stretched);[15] from fluorescence decay curves in An-LDPE and using DMA as quencher, we have found that E_D is also ca. 4 kcal/mol higher in the stretched films.[6]

Table 6. Activation energies from fluorescence growth curves for DAA out-diffusion from Py-LDPE films into methanol between 15 and 35°C.[15]

	E_a(kcal/mol)	
DAA	unstretched	stretched
DMA	12.7±0.5	16.9±0.7
DEA	9.2±0.4	11.7±0.5
DPA	8.0±0.5	9.1±0.6
DBA	6.0±0.8	a

a) No fluorescence intensity changes detected.

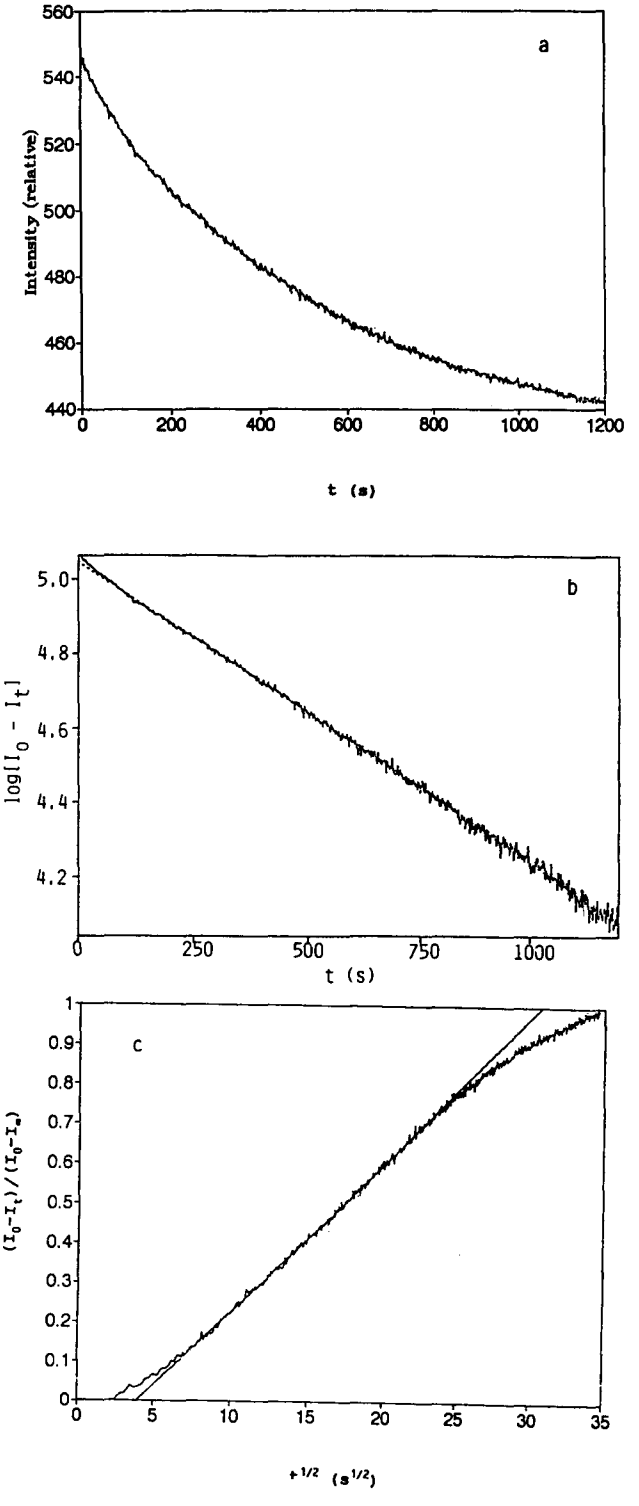


Figure 5. (a) Fluorescence decay curve from an unstretched An-LDPE film in contact with 0.95 M DMA in methanol at 22 °C. λ_{ex} 369 nm; λ_{em} 415 nm. (b) Data plotted according to eq. 3a. (c) Data plotted according to eq. 4a with a best linear fit to points between 0.2 and 0.7 along the ordinate.[6]

Any conclusion that it is easier for larger DAA molecules than for smaller ones to move within LDPE films must be qualified further by the previously mentioned data which shows that the fraction of pyrenyl-occupied sites which participate in the DAA-induced quenching decreases as the volume of a DAA molecule increases. Thus, it is more reasonable to ascribe the bizarre changes in activation energies to the set of sites being accessed becoming smaller as the DAA become larger; again, we conclude that there appears to be a distribution of sites, each with its characteristic free volume and accessibility.

In order to access a wider range of site types, we have developed methods which allow k and D values for DAA diffusion in native LDPE films to be measured.[17] In the first step, a molecule capable of fluorescence is doped into LDPE. It is then allowed to diffuse from LDPE and into a non-swelling liquid which contains an efficient quencher which does not enter LDPE. Thus, out-diffusion in these experiments leads to decay curves (Figure 6). Provided the quencher and liquid do not absorb at wavelengths where the dopant molecule is excited, treatment of the decrease in fluorescence intensity versus time according to eqs. 3a and 4a (where I_o and I_∞ now represent the maximum and minimum intensities, respectively) allows k and D to be calculated. Some characteristic values for DAA diffusion from LDPE into 2N HCl[18] are compared to data obtained using covalently modified films in Table 7.

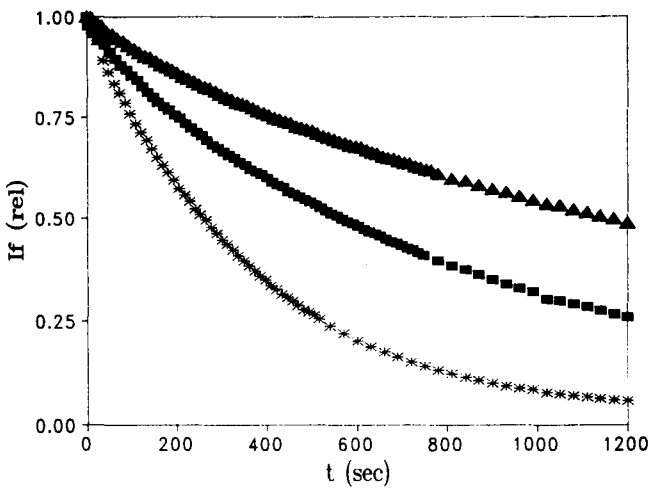


Figure 6. Fluorescence decay (out-diffusion) spectra from a native unstretched LDPE film, doped with DMA, in contact with 2N HCl at 15.0 (▲), 25.5 (■), and 34.0 °C (*).[18]

The activation energies, Ea and ED, derived from rate data using native unstretched LDPE according to eqs. 3 and 4 are collected in Table 8. They lead to a very different conclusion from that made on the basis of data in Table 6. The activation energies are higher and nearly constant throughout the series. The small decrease between DEA and DBA values can be rationalized on the basis of the lower overall concentration of the larger DAA in the film due to the smaller partition coefficient for DBA; if all doping procedures employ the same reservoir concentration of DAA, the film with DBA will have the lowest guest concentration at time = 0 in out-diffusion experiments. As a result, it will also have the smallest fraction of sites occupied. If these are the more accessible sites, it is not unreasonable that escape from them should be easier, also.

Table 8. Activation energies for DAA out-diffusion from native unstretched LDPE films into 2N HCl.[18]

DAA	E_D, kcal/mol	E_a, kcal/mol
DMA	15.1±0.3	14.5±0.1
DEA	15.2±0.4	14.7±0.1
DBA	13.4±0.1	13.7±0.1

The decrease in the differences among the activation energies reported in Table 8 (as compared to Table 6) can be explained, therefore, on the basis of site selection. The Py-LDPE and An-LDPE films allow a DAA molecule to enter only those sites which have a relatively voluminous lumophore covalently attached to it and which retain sufficient additional free volume. In the native films, all doped sites (i.e., potentially those with a minimum free volume equal to the van der Waals volume of one DAA molecule) contribute to the kinetics of diffusion. In fact, at early out-diffusion times, we have observed systematic deviations from single exponential decays of fluorescence intensity which may be due to loss of DAA molecules from very large sites with relatively unencumbered access routes to the film-liquid interface.

SUMMARY

We have described a series of experimental approaches to the characterization and, in some cases, exploitation of the dopant sites available in low density polythylene.

Although a full understanding of the distributions of shapes and free volumes of sites in LDPE films and the dynamics associated with them cannot be claimed yet, several conclu-

Table 7. Representative values of k and D for out-diffusion of DAA from native[18] and modified[6,7,15] unstretched LDPE films.

DAA	T(°C)	film type					
		native LDPE[a]		Py-LDPE[b]		An-LDPE[b]	
		k,s^{-1}	D,cm^2/s	k,s^{-1}	D,cm^2/s	k,s^{-1}	D,cm^2/s
DMA	25	$12x10^{-4}$	$0.90x10^{-8}$		0.8x10-8	$9.6x10^{-4}$	$1.8x10^{-8}$
	34	$28x10^{-4}$	$2.0x10^{-8}$				
	35			$12x10^{-4}$	$1.8x10^{-8}$	$18.0x10^{-4}$	$3.7x10^{-8}$
DEA	24	$3.8x10^{-4}$	$0.22x10^{-8}$				
	34	$8.8x10^{-4}$	$0.53x10^{-8}$				
	35			$7.1x10^{-4}$			
DPA	35			$5.9x10^{-4}$			
DBA	24.5	$2.3x10^{-4}$	$0.14x10^{-8}$				
	33	$3.5x10^{-4}$	$0.23x10^{-8}$				
	35			$4.7x10^{-4}$			

a) Receiving liquid is 2N HCl. b) Receiving liquid is methanol.

sions can be made: (1) the sites provided to dopant molecules are reduced in volume and the guests may change their location during film stretching; (2) the distribution of free volumes for sites in stretched films is much narrower than in unstretched ones; (3) the observed activation energies for diffusion of guest molecules is a convolution of their distribution in the film and the fraction of the total number of sites which are occupied.

It should be mentioned that our techniques should be amenable to the investigation of many types of polymers; efforts to apply them to other polymers have been initiated.

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REFERENCES

1. (a) Axelson, D.E.; Levy, G.C.; Mandelkern, L.; *Macromolecules,* (1979), **12**, 41. (b) Glenz, W.; Peterlin, A.; *Macromol. Sci. Phys.*, (1970), **B4**, 473. (c) Hadley, D.W.; In *Structures and Properties of Oriented Polymers*; Ward, I.M.; Ed.; Wiley: London, 1975, Chapter 9. (d) Nordmeier, E.; Lanver, U.; Lechner, M.D.; *Macromolecules,* (1990), **23**, 1072, 1077. (e) Renfrew, A.; Morgan, P.; *Polyethylene: The Technology and Uses of Polyethylene Polymers*, Interscience: New York, 1957.
2. Phillips, P.J.; *Chem. Rev.*, (1990), **90**, 425.
3. Others, using different approaches, have made important contributions to our understanding of the micromorphology of LDPE. See for example: (a) Atvars, T.D.Z.; Sabadini, E.; Martins-Franchetti, S.M.; *Europ. Polym. J.*, accepted for publication. (b) Meirovitch, E.; *J. Phys. Chem.*, (1984), **88**, 2629. (c) Hentschel, D.; Sillescu, H.; Spiess, H.W.; *Macromolecules,* (1981), **14**, 1605. (d) Yogev, A.; Riboid, J.; Marero, J.; Mazur, Y.; *J. Am. Chem. Soc.*, (1969), **91**, 4559. (e) Read, B.E.; *In Structure and Properties of Oriented Polymers*; Ward, I.M.; Ed.; Wiley: London, 1975, Chapter 4. (f) Gottlieb, H.E.; Luz, Z.; *Macromolecules,* (1984), **17**, 1959. (g) Yogev, A.; Margulies, L.; Amar, D.; Mazur, Y.; *J. Am. Chem. Soc.*, (1969), **91**, 4558. (h) Margulies, L.; Yogev, A.; *Chem. Phys.*, (1978), **27**, 89.
4. Michl, J.; Thulstrup, E.W.; *Spectroscopy with Polarized Light*; VCH: Deerfield Beach, FL, 1986.
5. Jang, Y.T.; Phillips, P.J.; Thulstrup, E.W.; *Chem. Phys. Lett.*, (1982), **93**, 66.
6. (a) He, Z.; Hammond, G.S.; Weiss, R.G.; *Macromolecules,* (1992), **25**, 1568. (b) He, Z. Ph.D. Thesis, Georgetown University, Washington, DC, 1991.
7. (a) Naciri, J.; Weiss, R.G.; *Macromolecules,* (1989), **22**, 3928. (b) Naciri, J.; Ph.D. Thesis, Georgetown University, Washington, DC, 1989.
8. Thulstrup, E.W.; Michl, J.; *J. Am. Chem. Soc.*, (1982), **104**, 5594.
9. (a) Aviv, G.; Sagiv, J.; Yogev, A.; *Mol. Cryst. Liq. Cryst.*, (1976), **36**, 349. (b) Hooker, R.H.; Rest, A.J., *Appl. Organometallic Chem.*, (1990), **4**, 141. (c) Uznanski, P.; Kryszewski, M.; *Polym. Bull.*, (1991), **26**, 437. (d) Li, S.K.L.; Guillet, J.E.; *Polym. Photochem.*, (1984), **4**, 21. (e) De Paoli, M.A.; de Oliveira, S.M.; Baggio-Saitovitch, E.; Guenzlanger, D..; *J. Chem. Phys.*, (1984), **80**, 730.
10. (a) Bichan, D.; Winnik, M.; *Tetrahedron Lett.*, (1974), **44**, 3857. (b) Mar, A.; Winnik, M.A.; *J. Am. Chem. Soc.*, *1985), **107**, 5376.
11. Ramesh, V.; Weiss, R.G.; *Macromolecules,* (1986), **19**, 1489.
12. (a) Bellus, D.; *Adv. Photochem.*, (1971), **8**, 109. (b) Meyer, J.W.; Hammond, G.S.; *J. Am. Chem. Soc.*, (1970), **92**, 2189.
13. (a) Bellus, D.; Schaffner, K.; Hoigne, J.; *Helv. Chim. Acta,* (1968), **51**, 1980. (b) Wang, Z.; Holden, D.A.; McCourt, F.R.W.; *Macromolecules,* (1990), **23**, 3773.
14. Cui, C., unpublished results.
15. Jenkins, R.M.; Hammond, G.S.; Weiss, R.G.; *J. Phys. Chem.*, (1992), **96**, 496.
16. Birks, J.B.; *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970, Chapter 9.
17. He, Z.; Hammond, G.S.; Weiss, R.G.; *Macromolecules,* (1992), **25**, 501.
18. Lu, L., unpublished results.