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New Methods for the Determination of Dopant Site Distributions and Dopant Rates of Diffusion in Low-Density Polyethylene Films with Covalently Attached Anthryl Groups: Fluorescence Quenching by *N,N*-Dimethylaniline in Unstretched, Stretched, and Swelled Films[1]

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ABSTRACT: Thermal decomposition of 9-anthryldiazomethane, doped into low-density polyethylene (LDPE) films, provides covalent attachment of anthryl groups at internal dopant sites. Fluorescence from the new material, An–LDPE, has been employed to measure the diffusion coefficients of *N,N*-dimethylaniline (DMA), its diffusion activation energy, and the relative distribution of dopant site sizes in unstretched, stretched, and swelled films. The results are compared with those from LDPE films containing covalently attached pyrenyl groups.

Introduction

In a previous study, we employed the product ratios from the competitive intramolecular Paterno–Buchi photocyclization and intermolecular photoreductions of 10-undecenyl benzophenone-4-carboxylate to probe the (microscopic) free volume changes that occur at dopant sites when films of low-density polyethylene (LDPE) are stretched (macroscopically).[2] The results—a marked increase in the relative yield of the photocyclization product when films were cold stretched to ca. 500% of their original length—indicate a surprisingly large decrease in the average free volume of dopant sites in the stretched films.

To confirm and quantify this conclusion, pyrenyl groups were attached covalently to LDPE polymethylene chains[3] at interior dopant sites. Then, the fraction of modified dopant sites which are capable of accepting at least one molecule of *N,N*-dimethylaniline (DMA), a diffusion-controlled quencher of pyrenyl fluorescence, was determined.[4] Again, the results indicated that film stretching reduces the average free volume of dopant sites: after equilibration with 0.95 M DMA in methanol at 25 °C, pyrenyl fluorescence intensities in unstretched and stretched films were reduced by 59% and 30%, respectively. Additionally, the pyrenyl–LDPE films were shown appropriate for measurement of rates of diffusion, diffusion coefficients, and activation energies for diffusion of noncovalently bound dopant molecules in the films.[4] A specific advantage of this method over others that place fluorophors along a polymer backbone[5] is that virtually all of the reporter groups are located away from the film surfaces.

Here, we report a new method involving carbene insertion reactions[6] for attachment of reporter groups to chains at interior sites in polymer films and demonstrate the utility of this material to study molecular diffusion. The system chosen links the 9 position of the anthryl groups through a methylene unit to polymethylene chains at LDPE dopant sites. It complements the pyrenyl–LDPE study in several ways: (1) the method of attachment is thermal (although a photochemical analogue can also be used); (2) the size of the dopant group is smaller; (3) the excited singlet state lifetime of the 9-anthryl group in hydrocarbon media ($\tau_F \sim 5$ ns[7]) is ca. 40 times shorter than that of pyrenyl,[7] allowing dynamic and static fluorescence quenching modes by noncovalently attached dopants to be differentiated.

The results obtained extend the scope of our investigations of the microscopic nature of polymer films, especially those composed of LDPE, by determining the influence of swelling and nonswelling solvents on the rates and efficiencies of the quenching of anthryl–LDPE (An–LDPE) fluorescence by DMA.

Experimental Section

Materials. Low-density polyethylene films were "Sclairfilm" 300 LT-1 (0.92 g/cm³, M_W 112 600,[8] 76 μm thick) supplied by Du Pont of Canada. Before use, films were immersed overnight in chloroform to remove antioxidants, washed with methanol, and dried in a stream of nitrogen. 9-Methylanthracene (Aldrich; 99%) was recrystallized from anhydrous ethanol and passed through a silica gel column (5/95 ethyl acetate/hexane as eluent) to yield material of mp 79.5–80.5 °C (lit.[9] mp 80–81 °C). *N,N*-Dimethylaniline (Aldrich; 99%) was distilled over activated zinc dust and stored under an N_2 atmosphere in a refrigerator until being used.[10] 2-(Dimethylamino)ethanol (DAE; Aldrich; 99%) was purified by Dr. Jawad Naciri[4,11] as suggested in the literature.[12] 9-Anthryldiazomethane (9ADM), decomposition ≥ 63 °C (lit. 63–64 °C,[13a] 64–66 °C[13b]), was synthesized from 9-anthrylaldehyde (Lancaster; 99%) via oxidation of the hydrazone, mp 122.5–124 °C (lit. 122–124 °C,[13a] 124–126 °C[13b]) according to the method of Nakaya et al.:[13a] IR (film on AgCl) 2054 cm⁻¹ (s); UV/vis (cyclohexane) λ_{max} 258, 320–450 nm (br). Diethyl ether (Fisher; reagent) was distilled from $LiAlH_4$ prior to use. All other solvents, HPLC or Photorex grade from Fisher or Baker, were used as received.

Preparation of LDPE Films with Covalently Linked Anthryl Groups (An–LDPE). After remaining in a chloroform bath for at least 24 h, a dried LDPE film was placed overnight in an ether solution of 9ADM. The 9ADM content was calculated from the UV/vis absorption spectrum of the doped film (using $\epsilon \simeq 10\,000$ at 400 nm[14]) and was either increased by bathing in a more concentrated 9ADM solution or decreased by placement in neat ether to reach ca. (1–5) × 10^{-3} M. After washing the film surfaces rapidly with methanol and drying with a stream of nitrogen, the film was flame-sealed in a small test tube. The tube was immersed in boiling methanol (T = 65 °C) for 2 h and broken, and the film was washed in two ether baths and several chloroform baths (≥30 min each) until the optical density (OD) of the film in the wavelength region of anthryl absorptions (300–400 nm) no longer changed. Assuming the ϵ values of 9-methylanthracene in cyclohexane (ϵ = 9600 at 368 nm) for the anthryl groups covalently linked to LDPE, average OD measurements of at least five different locations on the film indicated anthryl concentrations of (1.6–7.8) × 10^{-4} M in different preparations.

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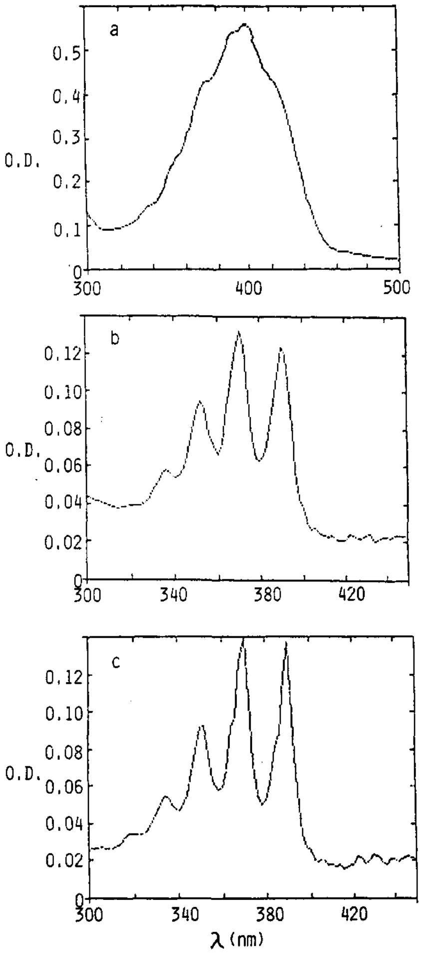

Figure 1. Representative UV absorption spectra: (a) an unstretched 9ADM/LDPE film before heating; (b) film in (a) after heating and exhaustive extraction with ether and chloroform (An–LDPE); (c) an unstretched 9MA/LDPE film. All spectra were recorded using an undoped LDPE film as reference. See text for details of procedures.

Usually, 20–25% of the initial 9ADM molecules became covalently attached by using this procedure.[15] Representative UV/vis absorption spectra are shown in Figure 1.

After covalent attachment of the anthryl groups, some LDPE films were cut into two strips and one piece was cold stretched by hand over a mandrel to ca. 500% of its original length. Upon release of tension, the stretched films shrank slightly (<10%). Only strips with a common origin were used to compare unstretched and stretched An–LDPE.

Methods. Emission and excitation spectra were obtained using a Spex Fluorolog spectrofluorometer (150-W high-pressure Xe lamp) interfaced to an IBM compatible 386SX AT computer. Data were analyzed with Quattro Pro using software written by Mr. Bill Craig. Films were held on a small glass yoke which was placed in a 1-cm^2 quartz cuvette.[11] The cuvette was held in a thermostating block connected to a circulating water bath. Temperatures within the cuvette could be maintained to ±0.5 °C.

For polarized fluorescence measurements (L formation single-channel method[16a]), one Glan Nicol prism was attached at the exit of the excitation monochromator (polarizer) and another was placed at the entrance to the emission monochromator (analyzer). The emission anisotropy (*r*) was calculated from fluorescence intensities (*I*) when the polars were in their four possible perpendicular and parallel orientations (eq 1, where $G = I_{hv}/I_{hh}$ and h and v are the horizontal and vertical axes of the polarizer and analyzer, respectively).[16]

$$r = (I_{vv} - I_{vh}G)/(I_{vv} + 2I_{vh}G) \qquad (1)$$

Linearly polarized absorption spectra were recorded at 25 °C on a dual-beam Perkin-Elmer 552 UV/vis spectrophotometer which had a Glan Nicol prism mounted vertically in the entrance port of both the sample and reference compartments. Films were sandwiched between quartz disks and held in fixed positions. *An unstretched or stretched film, oriented in the same vertical* direction as the doped film, was placed in the reference compartment. Dichroic ratios, $d = (\mathrm{OD}_{\parallel}/\mathrm{OD}_{\perp})_{\lambda}$ (where $\mathrm{OD}_{\parallel}$ and $\mathrm{OD}_{\perp}$ are the optical densities at wavelength λ when the polars are parallel (vertical) or perpendicular (horizontal), respectively, to the (vertical) direction of film draw), were calculated. For stretched films, the direction of stretch defined the orientation axes; for unstretched ones, two mutually perpendicular axes were defined as parallel and perpendicular. At least three OD determinations at each wavelength were averaged.

The degree of swelling by various solvents (Table I) was determined by laying a film in a flat-bottomed flask which was atop a square millimeter grid. The area of the film over the grid was measured, and sufficient solvent was added slowly to cover the film completely. Final swelling was assumed when the area of the film no longer increased during 1 h. The thickness increase was estimated by taking the square root of the area increase.

Diffusion and other experiments with DMA were conducted as described previously[4] except when the films were swelled. In those cases, the films on a glass yoke were preequilibrated with the solvent and the DMA in the same liquid was added to initiate the diffusion studies.

Results and Discussion

Low-density polyethylene (LDPE) can have many different structural characteristics[17] (i.e., its degree of branching and molecular weight) depending upon its method of manufacture and its thermal and mechanical histories. Usually, it consists of approximately equal amounts of amorphous and lamellar crystalline regions.[18] The amorphous part contains some short-chained branches (ca. 30 methyl groups per 1000 methylene groups[19]). Since the crystalline regions are virtually impermeable to dopants at room temperature,[20] swelling molecules tend to reside near branching points and along the lateral surfaces between crystalline and amorphous domains.[20b]

During the macroscopic stretching of LDPE films, the number of chains oriented along the axis of draw increases.[21,22] From ESR,[23] ^{2}H NMR,[24,25] and linear dichroism measurements[22,26] on dopant molecules and the polymer itself, there is strong evidence that film stretching aligns partially the chains of the amorphous region and allows dopant molecules residing nearby to experience a more-ordered environment. During the stretching process, some dopant molecules near branching points may also be translocated to the crystalline–amorphous interfacial regions.[20,23]

Characterization of An–LDPE Films. The most convincing evidence for the attachment of anthryl groups to LDPE films is our inability to diminish the intensity of the characteristic anthryl absorption (Figure 1) after films had been doped, heated, and extracted as described in the Experimental Section. When stored under a nitrogen atmosphere, the An–LDPE films could be used in our experiments during several months without evidence of change. LDPE films doped with 9-methylanthracene (9MA) suffered complete loss of their anthryl absorption after being washed several times in ether or chloroform.

Normalized excitation and emission spectra from an An–LDPE film, 9MA in LDPE, and 9MA in hexane are shown in Figures 2 and 3, respectively. The emission and excitation spectra of 9MA in hexane are shifted hypsochromically relative to those in LDPE; the absorption spectra of 9MA in the two environments follow the same relationship. We suspect that the shifts derive from the polarizability of LDPE being higher than that of hexane.[27] The lack of excimer emission in Figure 3 is expected because of the very low concentrations of anthryl groups

Table I
Swelling of an Unstretched An–LDPE Film ([An] = 6.5 × 10^{-4} M) by Various Solvents ($\Delta A/A$), Diffusion Coefficients (D) of DMA in the (Swelled) Film, the Fraction (F) of Anthryl Fluorescence Quenched by 0.95 M DMA in the Solvents (T = 25 °C), and Associated Diffusion Activation Energies (E_d)

solvent	volume per molecule, Å^3		$\Delta A/A$[c]	$D \times 10^7$,[d] cm^2/s	F[d,e]	E_d, kcal/mol
	a	*b*				
diethyl ether	85.5	172	0.12		0.46 ± 0.01	
hexane	113.3	217	0.12	6.7 ± 0.6	0.49 ± 0.03	5.6 ± 0.6
cyclohexane	100.0	179	0.17	5.0 ± 0.4	0.37 ± 0.01	3.8 ± 0.9
methanol/toluene (v/v)						
100/0 (stretched)				0.026 ± 0.001	0.12–0.21[f]	14.4 ± 1.0
100/0 (unstretched)			0	0.18 ± 0.02	0.34 ± 0.03	10.6 ± 0.5
90/10			0.02	0.61 ± 0.04	0.38 ± 0.01	
80/20			0.06	1.19 ± 0.05	0.42 ± 0.01	
60/40			0.09	1.9 ± 0.1	0.42 ± 0.01	
0/100	98.8	176	0.16	7.6 ± 0.6	0.36 ± 0.01	3.0 ± 0.1

[a] From Bondi's method of calculation.[32] [b] From molecular weights and densities at 20 °C. The large difference between the two modes of calculation is due to inefficient packing and thermal motions in the liquid which are not accounted for by Bondi's method.[32] [c] Area increase after swelling divided by the unswelled area of the film. Precision is ±0.02_5. [d] Average of three runs from decay curves. $F = 1 - I_{DMA}/I_0$ where I_{DMA} and I_0 are the background-corrected intensities of emission when the films were equilibrated with 0.95 M DMA in methanol and with methanol, respectively. [e] Corrected for residual solvent emission. [f] Uncorrected for the fact that [DMA] in stretched LDPE is 25% lower than that in an unstretched film;[4] from three stretched films.

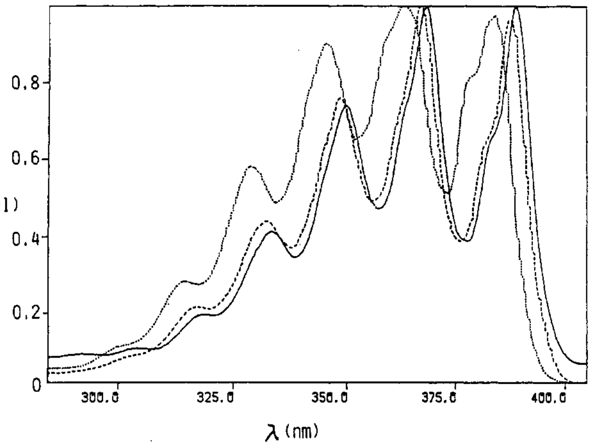

Figure 2. Normalized excitation spectra of an unstretched An–LDPE film ([An] = 6.5 × 10^{-4} M; λ_{em} = 415 nm, —), an unstretched 9MA/LDPE film ([9MA] = 6.8 × 10^{-4} M; λ_{em} = 414 nm, - - -), and (c) 7 × 10^{-5} M 9MA in hexane (λ_{em} = 410 nm, · · ·).

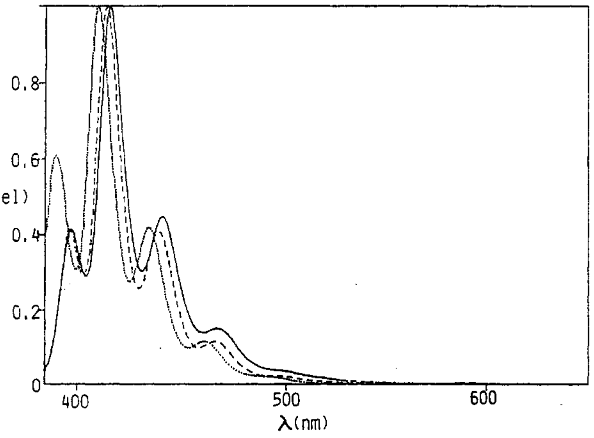

Figure 3. Normalized emission spectra of the An–LDPE film (—), the 9MA/LDPE film (- - -), and 9MA in a hexane solution (· · ·) described in Figure 2. λ_{ex} = 369 nm.

and their short excited singlet lifetimes;[7] only two anthryl groups residing in one dopant site could lead to excimer emission in the LDPE films. Its absence indicates that the precursor 9ADM molecules decompose primarily in singly-occupied sites.[28]

The fraction of anthryl groups in An–LDPE that are located away from the surface was determined by examining the intensities of emission from a film suspended in methanol in the absence and presence of 2 M 2-(dimethylamino)ethanol (DAE), a quencher of aromatic singlet states that reside near a film surface:[4] DAE is virtually insoluble in saturated hydrocarbons, and methanol is a nonswelling solvent for LDPE.[29] In methanol, 97% of the fluorescence of 5 × 10^{-6} M 9MA was quenched by 2 M DAE; the fluorescence intensities of unstretched and stretched An–LDPE films were decreased ~1% and ~2%, respectively, by the same DAE concentration. Thus, ≥98% of the anthryl groups in LDPE is inaccessible to the surface quencher.

Linear dichroic absorption spectra of stretched An–LDPE provide further information concerning the location of the anthryl groups. In addition to his assertion that molecules in amorphous regions of unstretched films can be translocated to the interfacial regions between amorphous and crystalline domains, Phillips also believes that dopants remaining in the amorphous region of stretched films will not be oriented anisotropically even though the chains surrounding them are at least partially oriented along the direction of draw.[20b] In films containing noncovalently linked dopant molecules, the possibility that translocation occurs makes an investigation of Phillips' prediction difficult. In our stretched An–LDPE films, the reporter groups cannot diffuse from the vicinity of the polymethylene chains near them in the unstretched state and groups originally in the amorphous region will remain there after film stretching.

An unstretched An–LDPE film ([An] = 4 × 10^{-4} M) and an unstretched film containing 9MA ([9MA] = 6.8 × 10^{-4} M) showed no linear dichroism (i.e., d = 1.00 ± 0.02 at ca. 260 and 390 nm). The stretched 9MA/LDPE film yielded d = 2.8 (260.5 nm) and 0.77 (391 nm). For the stretched An–LDPE film (Figure 4), d = 1.94 (261.5 nm) and 0.89 (392 nm). These absorption intensities are due almost exclusively to single transitions and are polarized along the long molecular axis (Z, from the ^1B_b transition at ca. 260 nm) and the short in-plane axis (Y, from the 0–0 band of the ^1L_a transition at ca. 390 nm).[22b] At such wavelengths, the dichroic ratio is related to O_f ($f = X, Y, Z$), the orientation factor, by eq 2.[22]

$$O_f \simeq d_f/(d_f + 2) \qquad (2)$$

On this basis, O_Z = 0.58 ± 0.01, O_Y = 0.28 ± 0.01, and O_X = 0.14 (by difference[22]) for the stretched 9MA/LDPE film; Thulstrup and Michl report O_Z = 0.51 and O_Y =

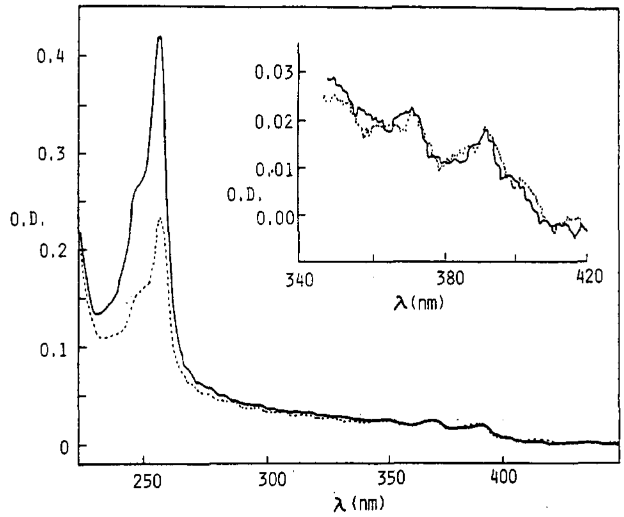

Figure 4. Polarized absorption spectra of a ca. 5× stretched An–LDPE film ([An] = 4 × 10^{-4} M) at room temperature: $OD_{\parallel}$ (—); $OD_{\perp}$ (···). A equally stretched undoped LDPE film was used as the reference.

0.29.[22c] We attribute the disparity between our and the reported O_Z values to differences in the constitutions of the films, the degrees of stretching, the concentrations of the 9MA, difficulties in locating accurately the base line at 260 nm, or a combination of these factors. Also, the $OD_{\parallel}$ and $OD_{\perp}$ at 390 nm were very small (see Figure 4 inset); the similarity between our O_Y and that reported previously for 9MA may be fortuitous. Regardless, our measurements are reasonably close to the reported ones and, as importantly, they are internally consistent: systematic errors will be constant for measurements on the 9MA/LDPE and An–LDPE films employed here; differences in O_f values between the two dopants are real. O_Z = 0.49 ± 0.01, O_Y = 0.30 ± 0.01, and O_X = 0.21 (by difference) from stretched An–LDPE. These variations may arise from the inability of covalently attached anthryl groups to translocate (supporting the Phillips prediction[20b]) or from orientational restrictions imposed by the methylene which links anthryl to an LDPE chain in An–LDPE films. In either case, the noncovalently and covalently attached reporter groups do not reside in equivalent sites within an LDPE film. Although slightly less oriented than their noncovalently linked counterparts, the anthryl groups of stretched An–LDPE films still sense acutely the directing influence of neighboring polymethylene chains.

Quenching of An–LDPE Fluorescence by Methanolic DMA in Unstretched and Stretched Films. Unlike DAE, DMA is relatively soluble in LDPE films. Using methods described previously for Py–LDPE,[4] we find that the partition coefficient for DMA, K, defined as the ratio of amine concentrations in An–LDPE and in methanol at equilibrium, is virtually constant in the temperature range examined: K = 0.20 ± 0.01 (unstretched). This value is within the experimental error of that measured for Py–LDPE films. We take K = 0.14 (stretched) as before.[4] Assuming that DMA molecules cannot enter the ca. 50% crystalline regions, the concentrations of DMA in the amorphous regions are 0.38 M (unstretched) and 0.29 M (stretched) if the initial quencher concentration in methanol is 0.95 M. However, for reasons mentioned previously, some parts of the amorphous regions are expected to accept dopant molecules more readily than others.

Since very little motion of a DMA can occur in LDPE during the excited singlet lifetime of an anthryl group, virtually all fluorescence quenching in An–LDPE films by DMA (which involves formation of an exciplex[7]) must be static (i.e., at least one DMA molecule must share an anthryl-occupied dopant site prior to excitation or no quenching will occur). When a DMA molecule is present, quenching of the excited anthryl group should proceed with unit efficiency since the quenching of anthracene fluorescence by DMA is diffusion-controlled in isotropic hydrocarbon solutions.[30] We assume reasonably that, even in a constrained environment, the anthryl group and DMA molecule will have adequate orientational flexibility to attain easily a quenching geometry.

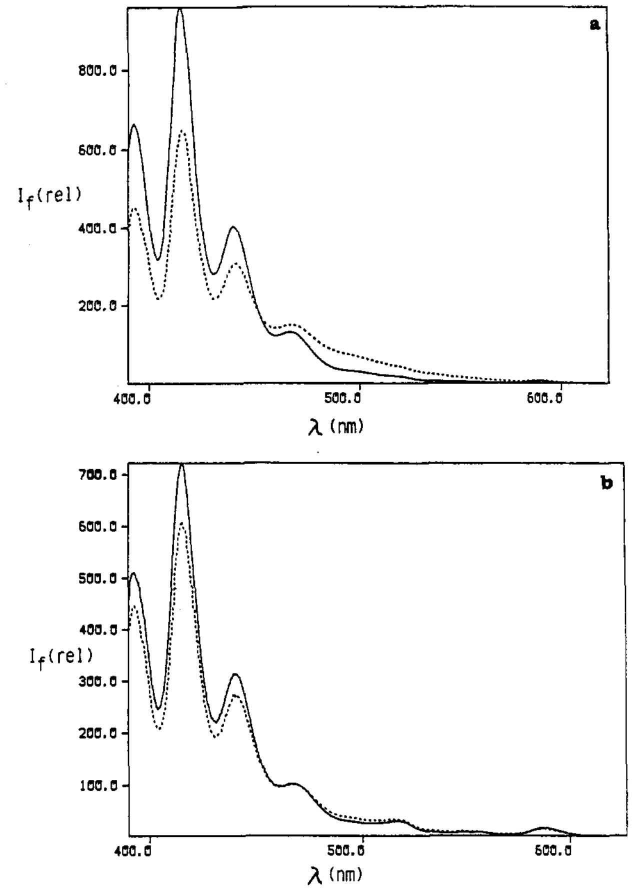

Figure 5. Relative intensities from emission spectra of an unstretched (a) and a stretched (b) An–LDPE film ([An] = 6.5 × 10^{-4} M) immersed in methanol (—) and after equilibration in a 0.95 M DMA in methanol solution (···).

The characteristics of pairs of unstretched and stretched An–LDPE films that share the same history were compared; due to the nature of their preparation, An–LDPE films from separate batches behave slightly differently. Essentially, a film was cut in two, and one piece was cold-stretched. Regardless of which An–LDPE film pair was used, fluorescence was always quenched much more in the unstretched part than in the stretched segment by a fixed concentration of DMA in methanol (for instance, see Figure 5). The results from three different film sets are included in Table II. The differences among F, the fraction of fluorescence quenched by DMA, for the three stretched films may be a consequence of our inability to stretch them in exactly the same way or of variations in the concentrations of anthryl groups within a film. We suspect the former since F should have differed for the unstretched films, also, if anthryl concentrations are critical. Regardless, the fractions of emission quenched by 0.95 M DMA are significantly lower than those found from Py–LDPE films whose F values, corrected for surface-accessible sites, are 0.53 (u) and 0.28 (s).[4] However, the

Table II
Comparative Quenching of Anthryl Fluorescence in Three Sets of Unstretched and Stretched An–LDPE Films by 0.95 M DMA in *Methanol* at 25 °C (λ_{ex} = 369 nm; λ_{em} = 415 nm)

film set	[An], M	type[b]	F^c	$F_u{}^d$
1	7.8×10^{-4}	u	0.34	0.34
		s	0.12	0.16
2[a]	6.5×10^{-4}	u	0.34 ± 0.03	0.34
		s	0.15 ± 0.01	0.20
3[a]	1.6×10^{-4}	u	0.35 ± 0.01	0.35
		s	0.21 ± 0.01	0.28

[a] Average of three runs. [b] u = unstretched; s = stretched. [c] $F = 1 - I_{DMA}/I_0$ where I_{DMA} and I_0 are the background-corrected intensities of emission when the films were equilibrated with 0.95 M DMA in methanol and with methanol, respectively. [d] F normalized to account for the different DMA concentrations in unstretched and stretched films.

qualitative conclusions from stretching either Py–LDPE or An–LDPE films is the same—*the average size of dopant sites in LDPE is reduced.*

One possible reason for the lower F values with An–LDPE is the difference between the excited singlet lifetimes of pyrenyl and anthryl groups. The much longer excited singlet lifetimes of pyrenyl groups could permit more dynamic quenching. Another possibility is that the types of sites occupied preferentially by a pyrenyl and an anthryl group may be different. This is quite plausible given the diverse methods by which the two groups were covalently attached to LDPE. However, much lower F values (0.37 for unstretched and 0.15 for stretched) have been measured for 0.95 M methanolic DMA and pyrenyl–LDPE films.[31] This suggests that variations in F should be expected from films prepared in different batches and may not depend solely upon the nature of the reporter group attached to LDPE or its volume and singlet lifetime. The smaller size of an anthryl group (245 Å^3 for 9MA[32]) as compared to that of a pyrenyl group (322 Å^3 [33]) should favor greater quenching of An–LDPE fluorescence since the minimum free volume required of a dopant site to accommodate both an anthryl group and one DMA molecule (128.5 Å^3) is roughly 375 Å^3 versus about 450 Å^3 for a pyrenyl group and one DMA molecule.[32-34] Thus, F values are most useful when being compared between an unstretched and a stretched film with shared histories or with one film and several diffusing species.[31]

Quenching of An–LDPE (Unstretched Film) Fluorescence by DMA in Swelling Solvents. The amount of each solvent in a saturated film was not directly determined in our experiments. We have assumed that the fractional swelling ability of the various solvents (Table I) is a measure of their (volume) concentrations in equilibrated films. On that basis we conclude that the acyclic molecules, ethyl ether and hexane, are less soluble in LDPE than are the cyclic hydrocarbons, cyclohexane and toluene. Also, the partition coefficients for DMA between LDPE and each of the solvents have not been determined. However, the similarity in molecular structure and polarity between hexane and cyclohexane leads us to believe that the partition coefficients for DMA between each of the solvents and a swollen film will be very similar. We have less intuitive feeling for the relative distribution proclivity of DMA between a film and the other two solvents, ethyl ether and toluene.

A deeper insight is gained from examination of the values of fractional fluorescence quenching of the bound reporter groups by DMA imbibed by the An–LDPE from the various solvents. At first glance, it is surprising that the greatest fractional quenching is observed with the two solvents, ethyl ether and hexane, which swell LDPE least. While we have no rigorous way to support the proposition, it is intuitively attractive to presume that the films which are swollen most contain the greatest concentrations of the quencher. If this is so, the results show that quenching efficiency does not follow the volume concentrations of quencher. Instead, we suggest that solvent molecules compete with DMA for occupancy of potential quenching sites adjacent to the fluorescent reporter groups. Since cyclohexane and toluene are closer to the size and shape of DMA than are hexane and ethyl ether, the cyclic solvents are expected to compete more efficiently.

To test further this hypothesis, the swelling of An–LDPE by methanol/toluene mixtures and the quenching of film fluorescence by DMA initially in these solvents were measured. Although swelling increases with the relative content of toluene in the mixtures (as expected), the values of F first rise and then fall; the change is small, but reproducible, and larger than our experimental error. The values of F increase initially with the concentration of toluene (and the mobility of DMA) in the film. However, the competition for space in anthryl-occupied dopant sites between toluene and DMA molecules becomes more acute as the concentration of toluene increases, leading to a decreased probability that a DMA molecule will be adjacent to an anthryl group at the moment of its excitation. Additionally, changes in the concentration of DMA in the An–LDPE film, resulting from variations in the solvent composition, may also influence the values of F.

Further evidence for the influence of swelling solvents on the dopant sites of LDPE occupied by anthryl groups comes from measurements of the anisotropy in linear dichroism emission. The emission anisotropy (r; eq 1) was determined for an An–LDPE film ([An] = 4.8×10^{-4} M) in methanol and in cyclohexane (Figure 6). The completely depolarized spectrum from 9MA in isotropic hexane is included. As can be seen, the unswelled film exhibits anisotropies that are more than twice those of the swelled one. Cyclohexane clearly increases the flexibility of polymethylene chains at a dopant site, allowing the anthryl groups greater rotational mobility, by occupying and expanding the free volume.

Diffusion Coefficients (D) of DMA in Unstretched and Stretched Films of An–LDPE. Fick's second law (eq 3) is used to describe the time dependence of uptake

$$M_t/M_\infty = (4/l)(D/\pi)^{1/2}t^{1/2} \tag{3}$$

of a dopant molecule by a film.[35] M_t and M_∞ are the dopant concentrations in the film at time = t and at equilibrium, respectively, l is the film thickness, and D is the diffusion coefficient for the dopant. D, as defined, is a function of film type, the medium "feeding" the dopant, and temperature. M_t/M_∞ is taken to be equal to the ratio of time-dependent fluorescence intensities at one wavelength in a film like An–LDPE[4,36] (eq 4, where I_0, I_t, and I_∞ are the

$$(I_0 - I_t)/(I_0 - I_\infty) = (4/l)(D/\pi)^{1/2}t^{1/2} \tag{4}$$

An–LDPE fluorescence intensities before the film comes into contact with a DMA solution, at time = t after contact, and when an equilibrium has been established between the film and the solution). The activation energy associated with the diffusion process is given by an Arrhenius-type equation (eq 5).[35,36] A typical plot of I_t versus time

$$D = D_0 e^{-E_d/RT} \tag{5}$$

for diffusion of DMA into an An–LDPE film is given in

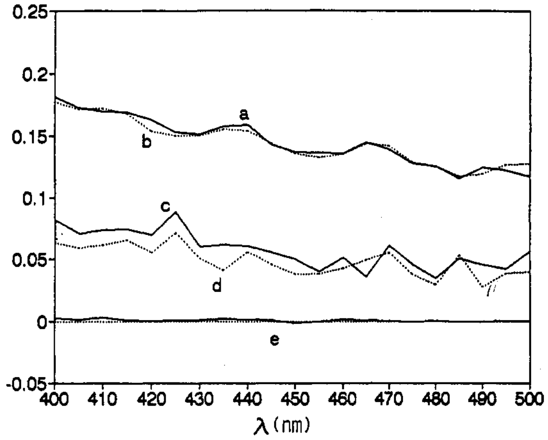

Figure 6. Emission anisotropies (r) versus wavelength (λ_{ex} = 369 nm) at 25 °C: (a,b) from an unstretched An–LDPE film ([An] = 4.8×10^{-4} M); (c,d) from the same film in cyclohexane; (e) from 7.0×10^{-5} M 9MA in hexane.

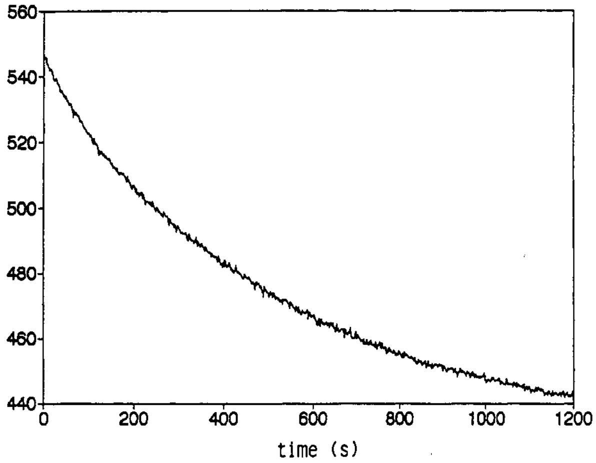

Figure 7. Representative decay curve of fluorescence intensity versus time at 22 °C from an unstretched An–LDPE film ([An] = 6.5×10^{-4} M) in 0.95 M DMA in methanol. λ_{ex} = 369 nm; λ_{em} = 415 nm.

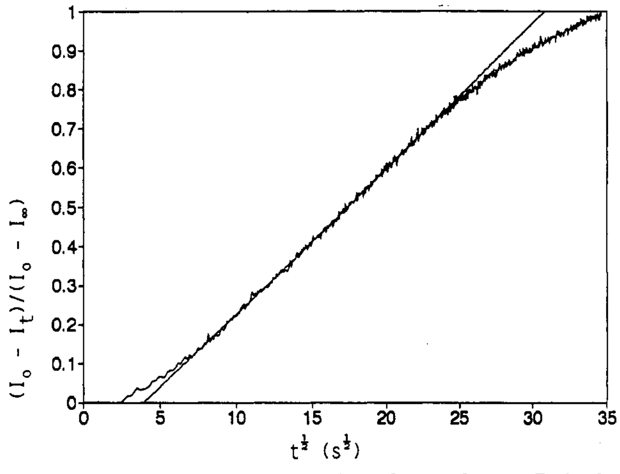

Figure 8. Data from Figure 7 replotted according to Fick's law as $(I_0 - I_t)/(I_0 - I_\infty)$ versus the half power of time. The best linear fit of points along the ordinate from 0.2 to 0.7 is shown, also.

Figure 7.[37] When replotted according to eq 4, Figure 8 is obtained. In all cases, D values were calculated from best linear fits to data in the range $0.2 \leq (I_0 - I_t)/(I_0 - I_\infty) \leq 0.7$ (i.e., the region where Fick's second law should apply). The diffusion coefficients for an unstretched and stretched An–LDPE film and the corresponding activation energies, E_d, are collected in Table III. In all cases, the films were preequilibrated with the neat solvent prior to placing them in contact with the 0.95 M DMA solution.

Table III
Diffusion Coefficients and Activation Energies for Diffusion from 0.95 M DMA Solutions into an AN–LDPE Film ([An] = 6.5×10^{-4} M)

solvent	T, °C	$D \times 10^8$,[a] cm²/s		E_d, kcal/mol
		unstretched	stretched	
methanol	15	1.1 ± 0.1	0.14 ± 0.02	10.6 ± 0.5 (unstretched)
	19	1.4 ± 0.3	0.18 ± 0.02	14.4 ± 1.0 (stretched)
	22	1.6 ± 0.1	0.22 ± 0.03	
	25	1.8 ± 0.2	0.26 ± 0.01	
	28	2.3 ± 0.3	0.33 ± 0.03	
	31	2.7 ± 0.1	0.53 ± 0.02	
	35	3.7 ± 0.3	0.68 ± 0.07	
hexane	15	56 ± 5		5.6 ± 0.6
	20	56 ± 5		
	25	67 ± 6		
	30	73 ± 6		
	35	92 ± 13		
cyclohexane	15	34 ± 4		3.8 ± 0.9
	20	44 ± 4		
	25	50 ± 4		
	30	52 ± 2		
	35	53 ± 6		
toluene	15	63 ± 6		3.0 ± 0.1
	20	69 ± 6		
	25	76 ± 6		
	30	82 ± 6		
	35	89 ± 13		

[a] Calculated by assuming a constant swelling change in thickness in each solvent from 15 to 35 °C.

Comparison of D values in methanol, a nonswelling solvent for LDPE, shows that DMA diffusion is nearly 1 order of magnitude slower in the stretched film and E_d is ca. 4 kcal/mol higher. Similar results were obtained for DMA diffusion in unstretched and stretched pyrenyl–LDPE films.[4] Although these numbers convey the sense that macroscopic stretching of an LDPE film slows dramatically the diffusion of a dopant molecule within it, they do not reflect totally the microscopic consequences. As mentioned previously, the fraction of anthryl singlets quenched at equilibrium by 0.95 M DMA in methanol is much larger for the unstretched film than for the stretched film. Even when the fractions are normalized to account for differing DMA concentrations within the two films at equilibrium, more quenching is calculated to occur from the unstretched one. Thus, not only is diffusion of DMA within the stretched film more difficult but the number of anthryl-occupied sites which can accept a DMA molecule is much lower: the activation energy reflects the ease (or difficulty) of entry by DMA molecules into those sites where quenching is feasible; a large number of anthryl-occupied sites are completely inaccessible due to the *much* higher energies that would be required for a DMA molecule to enter (i.e., their free volumes are inadequate to accommodate a DMA molecule, also).[38]

Alternatively, swelling of An–LDPE films by solvents facilitates DMA diffusion by increasing the mobility of chains within the amorphous regions and, probably, by expanding the free volume at dopant sites. As mentioned before and shown in Table I, greater facility of diffusion (as represented by D or E_d) is not always accompanied by more efficient quenching of anthryl groups (as represented by F) since the solvent molecules compete with DMA for space within a dopant site. Thus, hexane, cyclohexane, and toluene (three swelling solvents) lead to comparable D values of DMA at 25 °C which are 25–40 times greater than when methanol is the solvent; the E_d correlate roughly with the swelling ability of the solvents. At the same time, the fraction of An–LDPE fluorescence quenched by 0.95 M DMA in each of the four solvents differs by no more than ca. 30%.

Further evidence that this similarity is due to offsetting factors—the greater flexibility of the polymer chains and greater mobility of DMA in the swelled films versus the competition between DMA and swelling molecules for the dopant sites—is found in the methanol/toluene solvent mixture experiments reported in Table I. Although D at 25 °C increases regularly and E_d decreases, the fraction of An–LDPE fluorescence changes only slightly as the toluene content is increased. As mentioned previously, we attribute this to competition between DMA and toluene molecules for potential quencher sites.

Diffusion coefficients for hexane (1.256×10^{-8} cm^2/s), cyclohexane (0.607×10^{-8} cm^2/s), and toluene (1.813×10^{-8} cm^2/s) in LDPE at 25 °C have been reported.[39] They are comparable to the D of DMA in unswelled An–LDPE but are much smaller than the D of DMA after swelling. Clearly, the swelled An–LDPE film is a very different material from an unswelled film. Furthermore, the fact that the D values of the swelling solvents are much lower than that of DMA in the swelled films indicates that the medium traversed by DMA molecules within the swelled films has been "softened". However, diffusion does not occur along avenues comprised only of the swelling solvent since the coefficients of diffusion for molecules like hexane, cyclohexane, and toluene in solvents of like molecules are ca. 50 times larger than the D of DMA in swelled LDPE.[40]

Lastly, it is possible that the transfer of DMA molecules across the liquid/LDPE interface may play an important role in determining the D and E_d calculated here. Two limiting interface interactions can be envisaged: in the first, the liquid is a nonswelling, weakly interacting solvent (like methanol with LDPE); in the second, the liquid is a swelling, strongly interacting solvent (like cyclohexane or toluene). We have performed experiments which indicate that DMA transfer across interfaces of the former variety, at least, does not represent the critical step in the diffusion processes being measured here. An unstretched An–LDPE film ([An] = 4×10^{-4} M) was equilibrated as before with 0.95 M methanolic DMA at 25 °C. When placed in neat methanol at 25 °C, the calculated D value from the fluorescence growth curve, 1.6×10^{-8} cm^2/s, was very close to the value obtained previously from a decay curve, 1.8×10^{-8} cm^2/s. After redoping the film with DMA, it was placed at 25 °C in ~2 N HCl[41] and the D value obtained from the growth curve was 1.74×10^{-8} cm^2/s. Since water is a less-interacting solvent than methanol with LDPE, if the liquid/LDPE interfacial interactions were critical to the dynamics of out-diffusion, the D values should have differed by an amount which is much greater than our expected experimental accuracy. That they do not indicates that transfer of DMA molecules across an interface between a poorly interacting solvent and LDPE is a relatively facile step in the overall diffusion process.

Conclusions. We have made unstretched and stretched LDPE films with anthryl groups attached covalently at interior dopant sites. These materials complement the pyrenyl–LDPE films developed previously[4] in their utility and mode of preparation. They have been used to ascertain the average dopant site free volumes and diffusion characteristics of small noncovalently attached molecules. As found before,[4] accessibility of reporter groups to the quencher molecules is decreased by film stretching. From results with pyrenyl- and anthryl-modified LDPE films, it may be concluded that almost all of the quenching by DMA is static.

The films allow dynamic measurements of polymer diffusional properties to be measured in real time. The influence of swelling solvents on the mobility of DMA in LDPE and the size of dopant sites has been explored. The role of such solvents within a film is complex: they increase the rotational mobility of anthryl groups, decrease the energy required for diffusion, and compete with DMA quenching molecules for space in anthryl-occupied dopant sites. The dependence of DMA accessibility to anthryl-occupied dopant sites on the structure of the swelling solvent molecules was unanticipated and suggests that the film interiors are very selective in how they incorporate their guests.

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References and Notes

(1) This paper is dedicated to Professor Kurt Schaffner on the 60 ± 30 anniversary of his birth.

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Registry No. LDPE (homopolymer), 9002-88-4; 9ADM, 10401-59-9; DMA, 121-69-7.