valuable comments, and Dr. P. A. Sandford is thanked for linguistic corrections.

Registry No. 1, 9062-07-1; 2, 11114-20-8; 3, 9064-57-7.

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New Methods for the Determination of Dopant Site Distributions and Dopant Rates of Diffusion in Polymer Films: Emission from Pyrenyl Groups Covalently Attached to Low-Density Polyethylene[1]

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Received February 8, 1989; Revised Manuscript Received March 21, 1989

ABSTRACT: An adaptation of the method of Lamotte et al. (*J. Photochem.* **1987,** *38,* 177) is described for the covalent attachment of pyrene molecules to the interior of low-density polyethylene (LDPE) films. The modified polymers have been used to determine the relative distribution of dopant site sizes in unstretched and stretched films by measuring the fluorescence intensity of the pyrenyl groups in the absence and presence of pyrene, *N,N*-dimethylaniline (DMA), and (dimethylamino)ethanol. Dynamic partitioning of DMA between methanol and the films has been followed in real time by monitoring the fluorescence intensity from the pyrenyl groups. From these experiments, individual rate constants for flow of DMA into and out from unstretched and stretched LDPE films have been calculated. Activation energies for diffusion and diffusion coefficients have been calculated from the same data. They indicate that the barriers to DMA entering or exiting a film are nearly equal and do not depend upon film stretching provided the dopant site is large enough to accommodate both a pyrenyl group and a DMA molecule. However, the distribution of site sizes *is* altered upon film stretching. Pyrenyl fluorescence quenching by DMA is nearly halved when a film is stretched. This change is consistent with a dramatic decrease in the average free volume of dopant sites.

Introduction

Previously, we probed the changes that occur to the size and shape of dopant sites when films of low-density polyethylene (LDPE) are stretched.[2] By monitoring the ratio of cyclization to reduction products from irradiation of ω-undecenyl benzophenone-4-carboxylate in unstretched and stretched films, it was possible to ascertain that (macroscopic) stretching of the films results in a decrease in the average size of the solute-occupied (microscopic) sites. However, the magnitude of the decrease could not be ascertained from the available data. This and the photodimerization of tetraphenylbutatriene reported by Aviv et al.[3] are the only examples of which we are aware that compare the effect of stretching LDPE on dopant reactivity.

In somewhat related work, Gooden and co-workers[4] found that the ratio of Norrish I to Norrish II processes from irradiation of poly[ethylene-*co*-(carbon monoxide)] increases when the polymer is stretched. Also, Peterlin and Olf[5] compared the mobility of chain segments in unstretched and stretched polyethylene in the absence and presence of tetrachloroethylene. They observed by NMR spectroscopy that sorption increases chain mobility of unstretched, but not stretched, polyethylene.

Recently, Lamotte and co-workers[6] found that high-intensity irradiation of pyrene in hydrocarbon environments leads to 1-alkylated pyrenes. A two-photon mechanism involving an upper triplet state of pyrene was proposed to account for the reaction.[6b] In this paper, we demonstrate how the methodology of Lamotte and co-workers can be adapted to synthesize new polymeric materials that permit microscopic effects of macroscopically applied strain to be measured. The procedures and experiments are reported for one polymer,[7] LDPE, to which pyrenyl groups have been covalently attached at dopant sites.

In essence, the presence of highly fluorescent groups at fixed positions within LDPE films has permitted the approximate distribution of sizes of dopant sites, the rates of diffusion by *N,N*-dimethylaniline (DMA) into and out from the film (by a new technique), the fraction of pyrenyl groups near the surface, and the influence of film stretching on all of these to be determined in real time.

Experimental Section

Materials. Low-density polyethylene films were "Sclairfilm" 300LT-1 (0.92 g/cm^3, $\bar{M}_w$ 112 600,[8] 76 μm thick) supplied by Du Pont of Canada. Before use, film strips were immersed overnight in chloroform to remove antioxidants, washed with methanol, and then dried in a stream of nitrogen. Pyrene (Aldrich, 99%) was recrystallized three times from 95% ethanol and sublimed to yield mp 150–151 °C (lit.[9] mp 149–151 °C). DMA (Aldrich 99%), bp 85 °C (15 Torr), was purified according to the procedure of Meltzer and Tobolsky[10] and stored under nitrogen. 2-(Dimethylamino)ethanol (DAE, Aldrich, 99%) was dried over K_2CO_3 and fractionally distilled.[11a] The fraction with bp 134 °C (lit.[11b] bp 134 °C) was collected and stored under nitrogen. Methanol (Baker Photrex reagent) was used as received.

Preparation of Pyrenyl-LDPE Films. In a typical procedure, a strip of LDPE, 2 × 4 cm, was immersed overnight in a chloroform solution containing 0.24 M pyrene. The surface was rinsed thoroughly with methanol to remove any surface pyrene and the film was dried with a stream of nitrogen to remove any vestiges of chloroform. This created ca. 2.4×10^{-2} M dopant concentration of free pyrene (OD ~ 1 at 300 nm). The film was *suspended* inside a Pyrex test tube next to a 450-W Hanovia medium-pressure Hg arc and irradiated under nitrogen for 1 h. Due to the overlap of the broad spectral output of this lamp and the optical densities of pyrene at the various wavelengths, dopant molecules can be excited and covalently linked to polymethylene chains throughout the film thickness. The film was washed repeatedly in chloroform until UV absorption spectra of the washes showed no evidence of pyrene. The concentration of covalently linked pyrene ($\sim 4 \times 10^{-4}$ M) was then ascertained from an average of several UV absorption measurements at various locations on the dried film. The film was cut longitudinally in two and one piece was stretched over a smooth mandril to 400–500% its original length. When the stretching tension was released, the film exhibited a very small amount (<10%) of shrinkage.

Determination of Fluorescence Intensities with Time. Each covalently doped film strip was immobilized on a glass frame and placed in a cuvette containing a thermostated solution of DMA or DAE in methanol. Fluorescence intensities at 395 nm (monomer) or 443 nm (exciplex) (λ_{ex} 343 nm) were measured front-face as a function of time by using a Spex Fluorolog spectrofluorimeter equipped with a Datamate computer and a 150-W high-pressure Xe lamp. When the fluorescence intensity no longer changed perceptably with time, the solution was removed from the cuvette, and the film was washed rapidly with methanol. Then the cuvette was filled with pure, thermostated methanol, and the intensity of fluorescence was again monitored until it was constant.

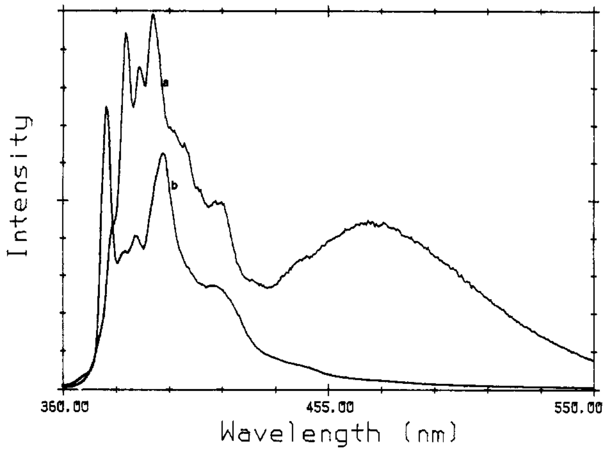

Figure 1. Room temperature emission spectra in air (a) from an LDPE film after immersion in a 0.24 M pyrene in chloroform solution for ca. 12 h and (b) from a doped film after irradiation for 1 h and exhaustive washing with chloroform. The spectra are not normalized; λ_{ex} 343 nm.

Equilibrium Constants for Partitioning DMA between Methanol and Pyrenyl-LDPE. Weighed LDPE films containing covalently attached pyrene were placed in 3.5-mL aliquots of thermostated solutions of DMA in methanol. After 1 h, the film was removed and washed rapidly with methanol. The DMA was extracted from the film by placing it in 3.5 mL of methanol for 1 h. Further washing with methanol showed no DMA. The concentration of DMA was determined from UV absorption spectroscopy in the methanolic bath.

Results and Discussion

Low-density polyethylene consists of lamellar crystalline and amorphous regions,[12] whose distribution is dependent upon the degree of short-chained branching, average molecular weight, and thermal and mechanical histories of the polymer.[13] Unstretched and unannealed LDPE (density 0.92 g/cm^3) contains about equal portions of amorphous and crystalline chains.[14] When films of LDPE are stretched macroscopically, the fraction of chains oriented along the axis of draw increases.[15,16] Furthermore, ESR,[17] ^{2}H NMR,[18] and linear dichroism[16,19] measurements provide convincing evidence that film stretching aligns partially the random chains of the amorphous region and allows dopant molecules residing nearby to experience a more ordered environment.

The locations of dopant sites in LDPE have been identified reasonably well. They occur preferentially near the less ordered branching points of polyethylene chains in the amorphous region and on the lateral surfaces of crystalline domains.[20] In both sites, the long axes of polycyclic aromatic molecules, like pyrene, lie preferentially parallel to neighboring polymethylene chains.[21]

Evidence for Covalent Attachment of Pyrenyl Groups to LDPE. Two major pieces of evidence confirm that the method of Lamotte and co-workers[6] affords *covalent* attachment of pyrenyl groups to the interior of LDPE films. Figure 1 presents the fluorescence spectra of films that were doped with pyrene (a) or were doped, irradiated, and then extracted with chloroform (b). The spectral shifts and vibronic intensity changes between the two spectra as well as between their corresponding absorption spectra are consistent with the presence of respectively unsubstituted and 1-alkylated pyrene moieties.[22] Thus, the sequence of steps leading to Figure 1b implies a clear chemical change in the dopant that is compatible with covalent attachment to a polymethylene chain. The loss of excimer emission ($\lambda_{max} \sim 470$ nm in Figure 1a) after irradiation and extraction of the doped film may indicate that only one of two pyrene molecules occupying a large dopant site can become covalently linked. A more likely explanation is based upon statistical considerations: the concentration of pyrenyl groups responsible for Figure 1b, $\sim 10^{-4}$ M, is more than an order of magnitude lower than in Figure 1a and may be insufficient to allow a reasonable fraction of the occupied dopant sites to contain more than one pyrene. It also raises the question whether *any* of the doubly occupied sites in Figure 1a lead to covalent attachment and emission in Figure 1b: excimer formation may quench the photochemical pathway to covalent attachment.

Physical evidence for covalent attachment of pyrene molecules to LDPE after irradiation of doped films comes from attempts to remove the dopant. Although all pyrenyl emission could be eliminated from unirradiated, doped films by chloroform extractions, a constant portion of emission (shown in Figure 1b) persisted in irradiated, doped films after exhaustive extractions. In fact, covalently doped films could be used in many experiments spanning several months before changes in their emissive properties became discernible. Were pyrene molecules somehow trapped mechanically within the LDPE films after irradiation, the spectral shifts mentioned above should not have been observed and the probes should have diffused slowly to the film surfaces.

The fraction of LDPE dopant sites that contain covalently linked pyrenyl groups is dependent upon the initial concentration of pyrene in chloroform during sorption, the radiation flux, and the irradiation time. In our experiments, we have attempted to incorporate covalently ca. 10^{-4} M pyrenyl lumophores into the LDPE. In spite of this, films prepared separately by seemingly the same procedures exhibit apparent differences in the fraction of dopant sites that contain a covalently linked pyrenyl group and the fraction of those sites whose remaining free volume can accommodate a second dopant molecule. For this reason, direct comparisons between unstretched and stretched pyrenyl-LDPE films are made only when the pair share a common history of preparation.

Characterization of Pyrenyl Attachment to LDPE Films. The method of attachment of pyrene molecules to the LDPE favors their being in the interior of the film: the films were washed with methanol prior to irradiation in order to remove surface-adsorbed pyrene.[16] By contrast, Whitesides[23] has developed methods that allow LDPE to be functionalized exclusively at or near a film surface.

To demonstrate that the pyrenyl groups are attached to the film interior, the fluorescence intensity of a pyrenyl-LDPE strip was measured after equilibration in methanol (a nonswelling solvent for LDPE[24]) and in 0.95 M 2-(dimethylamino)ethanol (DAE). DAE is quite insoluble in saturated hydrocarbons and, therefore, is expected to permeate the interior of LDPE to a very limited extent. However, virtually all of the fluorescence emanating from pyrenyl groups at or near the film surface should be quenched by 0.95 M DAE. Taking lower limit values of 100 ns for the singlet lifetime of surface-attached pyrenyl groups (τ_m) and 10^9 M^{-1} s^{-1} for the quenching rate constant (k_m) of pyrenyl groups in contact with the methanolic phase,[25] at least 99% of the surface-exposed lumophores should be quenched: $k_m[\mathrm{DAE}]/[k_m[\mathrm{DAE}] + (1/\tau_m)] \simeq 99\%$.

Table I

I_M/I_E Ratios from Unstretched (u) and Stretched (s) LDPE Films Soaked in 0.24 M Pyrene in Chloroform at Room Temperature

film pair	I_M/I_E					
	first doping			second doping		
	u	s	s/u	u	s	s/u
1	3.7 ± 0.3	7.1 ± 0.4	1.9	2.5 ± 0.2	10.0 ± 1.0	4.0
2	2.2 ± 0.1	7.1 ± 1.7	3.2	3.0 ± 0.3	3.5 ± 0.2	1.2
3	4.4 ± 0.4	10.9 ± 0.6	2.5	4.3 ± 0.1	15.0 ± 1.0	3.5
av			2.5			2.9

From the very small decreases in fluorescence intensity found in the unstretched (ca. 3% and 6%) and stretched (ca. 2% and 5%) films from two different preparations, we conclude that very few pyrenyl groups reside near a film surface. The ratio of surface area to volume (A/V) in the unstretched film was 2.2×10^2 cm^{-1}. This ratio increased ca. 2.2 times when the film was stretched to 400% of its original length. If the pyrenyl groups were evenly distributed throughout the film, an increase in A/V should cause a corresponding change in the number of pyrenyl groups that are exposed at the surface. The results indicate that the pyrenyl groups are located rather deep within the films and remain so after macroscopic stretching.

Qualitative Measures of the Influence of Film Stretching on the Distribution of Dopant Site Sizes in Pyrenyl-LDPE. The different dopant sites of unstretched and stretched LDPE were categorized on the basis of their size and accessibility to noncovalently linked pyrene in a series of manipulations.

In the first set of experiments, qualitative differences in the fraction of dopant sites of unstretched and stretched LDPE whose free volumes are at least 645 Å^3 (i.e., the van der Waals volume of two pyrene molecules[26]) were determined by monitoring the ratio of emission intensities from pyrene monomers and excimers. A strip of LDPE that had been doped with pyrene and irradiated as before was cut in two. Before the noncovalently bound pyrene was removed, one of the strips was stretched and the emission spectrum from each was measured in air at six to nine different parts. From these, the average monomer to excimer emission intensity ratios, I_M/I_E ($=I_{392}/I_{470}$; λ_{ex} 343 nm), in the film pieces were found to be 1.9 ± 0.2 (unstretched) and 3.5 ± 0.3 (stretched). The free pyrene was leeched thoroughly from the films with chloroform and then added again (bathed in a 0.24 M pyrene in chloroform solution overnight). The I_M/I_E ratios were remeasured and found to be similar to those found initially: 2.0 ± 0.1 (unstretched) and 5.0 ± 0.5 (stretched). The unstretched piece was then stretched, resulting in an increase in I_M/I_E to 3.5 ± 0.1.

Changes in the sizes of dopant sites can be detected in the absence of covalently linked pyrene also. When a film of LDPE was doped with noncovanelty linked pyrene as before, and one-half was stretched, the I_M/I_E ratio was larger in the stretched piece. Exhaustive cleaning of the two pieces from the same film in chloroform followed by redoping in another 0.24 M pyrene in chloroform solution led to the same qualitative relationship between the I_M/I_E ratios of the unstretched and stretched pieces. The values of I_M/I_E from three different pairs of LDPE strips are presented in Table I. In these experiments, the film surfaces were washed with methanol and films were dried before emission spectra were recorded. The lack of good

Table II
Relative Pyrenyl and Exciplex Emission Intensities[a] for Unstretched and Stretched Pyrenyl-LDPE Films Equilibrated at 25 °C for 30 min in Methanol and in 0.95 M in DMA in Methanol[e]

	unstretched			stretched		
run	I_1^{MeOH} [b]	I_1^{DMA} [c]	I_3 [d]	I_1^{MeOH} [b]	I_1^{DMA} [c]	I_3 [d]
1	9.61×10^5	3.37×10^5	1.62×10^5	5.94×10^5	4.25×10^5	4.72×10^4
2	12.98×10^5	6.67×10^5	1.70×10^5	6.00×10^5	4.35×10^5	4.92×10^4
3	7.62×10^5	3.49×10^5	1.56×10^5	5.14×10^5	4.18×10^5	4.96×10^4

[a] λ_{ex} 343 nm. [b] $I_1^{\mathrm{MeOH}} = I_{395}^{\mathrm{MeOH}} - I_{360}^{\mathrm{MeOH}}$. [c] $I_1^{\mathrm{DMA}} = I_{395}^{\mathrm{DMA}} - 3.4 \times 10^4$. [d] $I_3 = I_{443}^{\mathrm{DMA}} - \dfrac{(I_{395}^{\mathrm{DMA}} - 3.4 \times 10^4)(I_{443}^{\mathrm{MeOH}} - I_{360}^{\mathrm{MeOH}})}{(I_{395}^{\mathrm{MeOH}} - I_{360}^{\mathrm{MeOH}})}$. [e] $I_{395} = 3.4 \times 10^4$ and $I_{443} = 5.8 \times 10^3$ for 0.95 M DMA in methanol without a film present.

quantitative agreement between the experiments can be attributed to a combination of our inability to dope films in an exactly reproducible fashion, differences in surface reflectivity, and perhaps a lack of homogeneity in the spatial distribution of dopant sites within a film.

Regardless, the trends from the results in Table I demonstrate that the cycle of film doping does not alter appreciably the access to whatever dopant sites are present: the stretched to unstretched ratios (s/u) from the first and second doping procedures are clearly within the large limits of experimental error. Perhaps more importantly, both I_M/I_E results from the pyrene/pyrenyl-LDPE experiments and from Table I lead us to conclude that *film stretching decreases the average size of dopant sites.* This observation is in accord with our prior studies that employed a completely different analytical approach.[2]

Quantitative Measures of the Influence of Film Stretching on the Distribution of Dopant Site Sizes in Pyrenyl-LDPE. A more quantitative measure of the influence of film stretching on dopant site sizes is available from studies that compare fluorescence intensities of pyrenyl-LDPE films in the absence and presence of *N,N*-dimethylaniline (DMA), a quencher of pyrenyl singlets that is quite soluble in LDPE and that absorbs and emits only weakly at the wavelengths monitored. Thus, unstretched and stretched pyrenyl-LDPE strips were immersed in methanol and their fluorescence intensities were measured. As with DAE, the methanol was replaced with a solution of 0.95 M DMA in methanol. The fluorescence intensities were recorded after 30 min, a period that allows the partitioning of DMA between methanol and LDPE to reach equilibrium. By subtraction of the small contribution of DMA fluorescence from the intensities at 395 nm and the residual components of pyrenyl fluorescence from the largely exciplex emission at 443 nm, corrected relative intensities for monomer and exciplex emissions (I_1^{DMA} and I_3, respectively) from DMA-equilibrated films and I_1^{MeOH} from DMA-free films were calculated (Table II). The intensities were ratioed according to eq 1–3 in order to

$$\frac{[I_3/I_1^{\mathrm{MeOH}}]_u}{[I_3/I_1^{\mathrm{MeOH}}]_s} = \frac{\chi_u}{\chi_s} \tag{1}$$

$$\frac{[I_3/I_1^{\mathrm{DMA}}]_u}{[I_3/I_1^{\mathrm{DMA}}]_s} = \frac{\chi_u/(1-\chi_u)}{\chi_s/(1-\chi_s)} \tag{2}$$

$$\frac{[I_1^{\mathrm{DMA}}/I_1^{\mathrm{MeOH}}]_u}{[I_1^{\mathrm{DMA}}/I_1^{\mathrm{MeOH}}]_s} = \frac{1-\chi_u}{1-\chi_s} \tag{3}$$

calculate χ_u and χ_s, the fractions of pyrenyl sites in unstretched and stretched films that include at least one DMA molecule.

The minimum volume necessary to accommodate a pyrenyl group and one DMA molecule (ca. 450 Å^3 [26,27]) is somewhat smaller than that required for two pyrene molecules (645 Å^3 [26]), and therefore, fluorescence from a greater fraction of pyrenyl groups should be quenchable by DMA than by pyrene. Due to the overlapping emission spectra from bound and free pyrene (and their excimers), a detailed analysis of the fraction of the fluorescence from bound pyrenyl groups quenched by pyrene could not be made.

The three pairwise solutions to eq 1–3 were in excellent agreement. They led to average values for $\chi_u = 0.59$ and $\chi_s = 0.30$ that deviated by no more than 0.02. These χ are the sum of the fraction of *internal* pyrenyl sites that contain at least one DMA molecule (χ^{in}) and the fraction of pyrenyl sites that are at or near a film surface (χ^{ex}) in unstretched (u) and stretched (s) films. The latter fraction is available from experiments conducted with DAE: $\chi^{\mathrm{ex}} \simeq \chi^{\mathrm{DAE}}$ and $\chi = \chi^{\mathrm{in}} + \chi^{\mathrm{ex}}$. Since it is the internal sites in unstretched and stretched films that we wish to compare, $\chi_u - \chi_u^{\mathrm{DAE}}$ and $\chi_s - \chi_s^{\mathrm{DAE}}$ were calculated. Thus, $\chi_u^{\mathrm{in}} = 0.53$ and $\chi_s^{\mathrm{in}} = 0.28$.

Before these values can be compared directly, one further factor must be considered. The concentration of DMA in stretched films is only 70% of that in unstretched ones (vide infra). To bring χ_u^{in} and χ_s^{in} to the same quenching conditions, χ_u^{in} has been multiplied by 0.7.[28] Thus, at equal quencher concentrations within the film, one-third more pyrenyl sites contain at least one DMA molecule in the unstretched films than in the stretched one.

Diffusion in Pyrenyl-LDPE Films. In homogeneous media that mimic the polarity characteristics of LDPE, DMA is known to quench pyrenyl fluorescence at near-diffusion-controlled rates while forming an emissive exciplex.[29] The dynamic partitioning of DMA between LDPE and methanol was measured by using this experimental marker and the temporal intensity changes it causes to the fluorescence from pyrenyl groups attached at LDPE dopant sites. The temperature range over which experiments were conducted, 19–35 °C, is known to be free of polymer phase transitions and annealing effects for long periods.[5,30] No phase transitions were observed between 0 and 100 °C by differential scanning calorimetry for a sample of Sclairfilm or for unstretched and stretched pyrenyl-LDPE films. For the latter, the endotherm maximum occurred at 114.5 °C (unstretched) and 113.5 °C (stretched).

Figure 2 shows normalized emission spectra from a pyrenyl-LDPE film suspended in methanol and equilibrated in the absence (a) and presence (b, c) of 0.95 M DMA. The broad shoulder at λ ~ 443 nm is due to the exciplex. We assume that emission intensity at any wavelength is primarily static since the excited singlet lifetime of pyrene is <450 ns[29] and diffusion across the film occurs on a time scale of minutes.[31]

DMA-induced time-dependent intensity changes in pyrenyl-LDPE fluorescence were obtained in two ways. In the first, a 2.8-mL aliquot of a DMA–methanol solution was placed rapidly in a cuvette containing a suspended film and the fluorescence intensity (decrease) was monitored

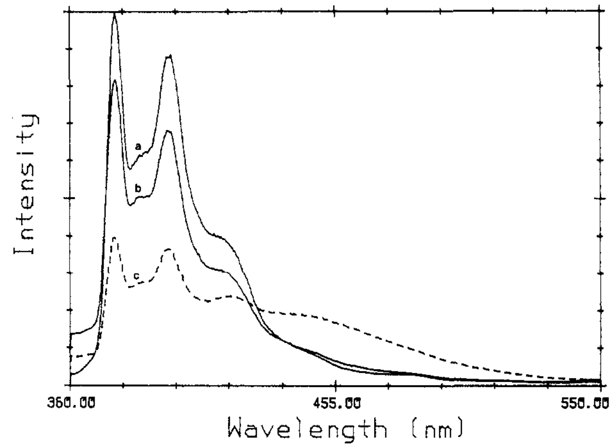

Figure 2. Room temperature emission spectra of (a) an unstretched or stretched pyrenyl-LDPE film in methanol (normalized to equal intensity) and the stretched (b) and unstretched (c) pyrenyl-LDPE films in a 0.95 M DMA in methanol solution after 30 min. The spectral intensities of (b) and (c) are relative to the corresponding spectrum of (a). All solutions are N_2 saturated; λ_{ex} 343 nm.

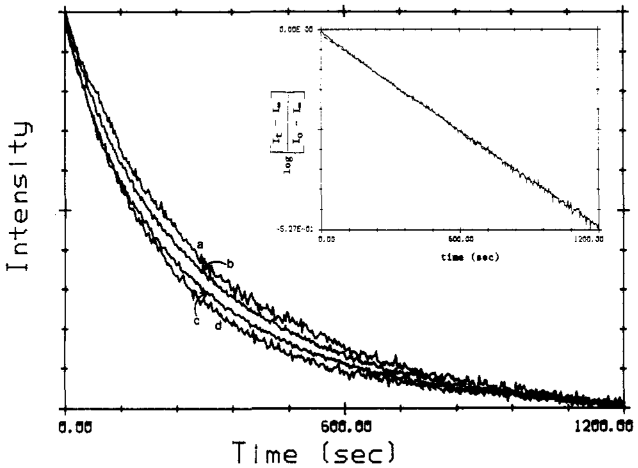

Figure 3. Fluorescence decay curves from an unstretched pyrenyl-LDPE film at 28 °C (λ_{em} 395 nm; λ_{ex} 343 nm) in N_2 saturated methanol containing (a) 0.5 M DMA, (b) 0.65 M DMA, (c) 0.8 M DMA, and (d) 0.95 M DMA. The inset displays the logarithmic intensity changes versus time from (a) and the best linear fit.

continuously at 395 nm as a function of time until no further changes could be detected (ca. 10–50 min). Examples of the decay curves so obtained are presented in Figure 3. In the second method, the solution from the above experiment was removed from the cuvette, the film was washed rapidly with methanol to remove DMA on the surface, and 2.8 mL of pure methanol was added. Fluorescence intensity (increases) were followed again at 395 nm as a function of time until no changes were detected. The growth and decay curves from one piece of film at an initial concentration of DMA and a fixed temperature could be reproduced (±5%) over many cycles. Therefore, the first entering DMA does not appear to open permanent channels that accelerate the entry and departure of other molecules. This quantitative conclusion is in accord with the qualitative one derived from studies with pyrene as the diffusing molecule.

Contrary to the I_M/I_E ratios that are a function of the various degrees to which pyrenyl groups are linked to different dopant sites in a particular film (vide ante), diffusional rates for DMA are a property of the type of LDPE from which samples were prepared. The rates were reproducible quantitatively (±10%) between films that had been prepared separately. The small variations in rates from different films were systematic, so that the derived activation energies (vide infra) were quite similar.

Table III
Equilibrium (Partitioning) Coefficients for DMA between Methanol and Pyrenyl-LDPE[a]

	T, °C		
	20	30	40
$K(u)$	0.19 ± 0.1	0.21 ± 0.01	0.21 ± 0.01
$K(s)$	0.15 ± 0.01	0.13 ± 0.01	0.13 ± 0.01

[a] Each number is an average K obtained from five different total DMA concentrations.

For all initial concentrations of DMA ≥ 0.5 M and all temperatures greater than 19 °C, the decay and growth curves could be fit very well to a single exponential expression. However, in some cases, there was a hint of a second, faster component. Its presence was confirmed from experiments conducted with lower initial DMA concentrations and at lower temperatures. We believe that the faster component is related to the small fraction of pyrenyl groups attached near the film surface: if first equilibrated with methanolic DAE, a pyrenyl-LDPE film treated incrementally with DMA displayed fluorescence intensity decay curves in which the fast component was nearly eliminated. Our analyses of dynamic data will concentrate on the major (slower) component of fluorescence intensity change.

A simple model for DMA partitioning between methanol and LDPE can be expressed as an equilibration between two environments (eq 4, where DMA_M and DMA_P are DMA in methanol and LDPE, respectively). The rate

methanol | LDPE

$$\mathrm{DMA_M} \underset{k_{out}}{\overset{k_{in}}{\rightleftharpoons}} \mathrm{DMA_P} \qquad (4)$$

expression that describes the movement of DMA from one environment to the other is given by eq 5. It assumes equal accessibility of DMA molecules to all dopant sites that contain quenchable pyrenyl groups and no dissociation of the exciplexes (i.e., once a DMA molecule enters a dopant site, it remains there for a period that is much longer than the singlet lifetime of a pyrenyl lumophore).

When the net flow of DMA is zero ($d[DMA]/dt = 0$), $K = k_{in}/k_{out}$ is given experimentally by the ratio $[DMA_P]^\infty/[DMA_M]^\infty$, the concentrations at equilibrium (infinite time). Values of $[DMA_P]^\infty$ were obtained by extracting into methanol all of the DMA from a pyrenyl-LDPE film of known volume and measuring the concentration of DMA by UV/vis absorption spectroscopy. Since the actual quantity of DMA_P was always < 1% of that of DMA_M, K was taken to be $[DMA_P]^\infty/[DMA_M]^0$, where $[DMA_M]^0$ is the concentration of DMA initially placed in methanol prior to equilibration. The values of K so obtained were independent of $[DMA_M]^0$ in the range 0.3–0.95 M. Equally important, plots of $[DMA_P]^\infty$ versus $[DMA_M]^0$ could be extrapolated linearly to zero intercepts for all of the temperature range investigated. The values of K for unstretched and stretched films are collected in Table III.

$$d[DMA_M]/dt = -k_{in}[DMA_M] + k_{out}[DMA_P] \qquad (5)$$

If all of the DMA is placed initially ($t = 0$) in the methanol, $[DMA_P]^0 = 0$ and the integrated form of eq 5 is eq 6. Also,

$$\ln\left[\frac{K[DMA_M] - [DMA_P]}{K[DMA_M]^0}\right] = -(k_{in} + k_{out})t \qquad (6)$$

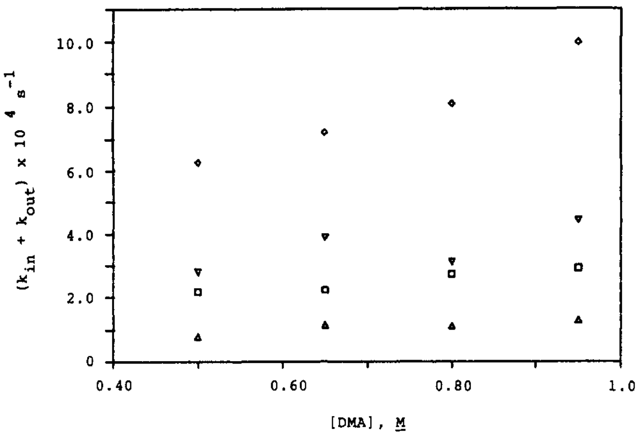

Figure 4. $k_{in} + k_{out}$ of DMA from fluorescence decay curves for unstretched (□, ◇) and stretched (△, ▽) pyrenyl-LDPE films versus initial DMA concentration in methanol at 19 °C (□, △) and 31 °C (◇, ▽).

since $[\mathrm{DMA_M}] \simeq [\mathrm{DMA_M}]^0$ at all times, eq 6 can be simplified to eq 7.

$$\ln\left[1 - \frac{[\mathrm{DMA_P}]}{K[\mathrm{DMA_M}]^0}\right] = -(k_{in} + k_{out})t \qquad (7)$$

A key to our work is that $[\mathrm{DMA_P}]$ can be expressed in terms of fluorescence intensities as shown in eq 8. Substituting this expression into eq 7 yields eq 9, which predicts that the sum of the rate constants for DMA partitioning can be obtained from plots of ln $[I_f - I_f^\infty]$ versus time. As mentioned above, such plots do yield linear slopes. The individual rate constants are then obtained from their ratio (available as K) and sum.

$$[\mathrm{DMA_P}] = \frac{I_f^0 - I_f}{I_f^0 - I_f^\infty}[\mathrm{DMA_P}]^\infty \qquad (8)$$

$$\ln\left[\frac{I_f - I_f^\infty}{I_f^0 - I_f^\infty}\right] = -(k_{in} + k_{out})t \qquad (9)$$

If the second set of limiting experimental conditions (i.e., $[\mathrm{DMA_M}]^0 = 0$ and $[\mathrm{DMA_P}] = [\mathrm{DMA_P}]^0$) is imposed, eq 10, whose form is analogous to eq 9, can be derived. Since the fluorescence growth curves are predicted to provide another determination of $k_{in} + k_{out}$, some details about the model can be scrutinized.

$$\ln\left[\frac{I_f^\infty - I_f}{I_f^\infty - I_f^0}\right] = -(k_{in} + k_{out})t \qquad (10)$$

In fact, small differences between $k_{in} + k_{out}$ are found when decay (eq 9) and growth (eq 10) curves of fluorescence intensity are analyzed. These appear to derive from the influence that large concentrations of DMA have on the properties of methanol as a solvent. As shown in Figure 4, the calculated sums of $k_{in} + k_{out}$ are independent of $[\mathrm{DMA_M}]^0$, as expected.

Due to the absence of large amounts of DMA in methanol, we have greater confidence in $k_{in} + k_{out}$ sums derived from fluorescence growth curves using pyrenyl-LDPE films doped initially with varying amounts of DMA. Representative Arrhenius plots constructed from these k_{in} and k_{out} for unstretched and stretched films are presented in Figure 5. The rate constants are available as supplementary material; their correlation coefficients are always > 0.995.

The activation energies are summarized in Table IV. Since K is constant over the temperature range for which $k_{in} + k_{out}$ was determined, the activation energies associated with k_{in} and k_{out} (ΔE^*_{in} and ΔE^*_{out}, respectively) must also be equal. We consider that all of the activation energies derived from either decay or growth curves are within the true experimental (accuracy) error of each other: the error limits shown represent the precision of data taken over a relatively small temperature range. Thus, differences between the rate constants k_{in} and k_{out} derive from preexponential (entropic) factors; the enthalpic barriers for DMA molecules to diffuse from or to a dopant site are equal.

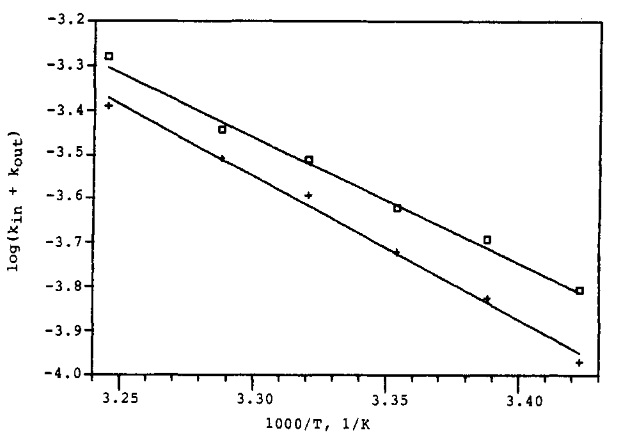

Figure 5. Representative Arrhenius plots for $k_{in} + k_{out}$ of DMA from fluorescence growth curves of unstretched (□) and stretched (+) pyrenyl-LDPE films (in methanol) that had been preequilibrated with 0.5 M DMA in methanol.

Table IV
Activation Energies for Movement of DMA between Methanol and Pyrenyl-LDPE

LDPE	$\Delta E^*_{\text{in or out}}$, kcal/mol,[a] for $[\mathrm{DMA}]_M^0$ (M)[b] 0.50	0.65	0.80	0.95	av
unstretched					
from decay	16.5 ± 0.6	17.0 ± 0.5	16.1 ± 0.8	18.5 ± 0.8	17.0
from growth	13.1 ± 0.5	13.9 ± 0.5	11.9 ± 0.3	13.2 ± 0.5	13.0
stretched					
from decay	17.7 ± 0.8	18.6 ± 0.6	15.0 ± 0.3	18.5 ± 0.2	17.5
from growth	14.8 ± 0.6	14.4 ± 0.3	13.2 ± 0.5	14.5 ± 0.2	14.2

[a] All correlation coefficients ≥ 0.995. [b] Initial DMA concentration.

The growth curve derived activation energies from unstretched LDPE are consistently ca. 1 kcal/mol smaller than from stretched LDPE. We are reluctant to ascribe any physical significance to this difference since the unstretched and stretched values are near the limits of precision error and, as mentioned above, the accuracy error is probably somewhat larger. Subsequent calculations will be based exclusively upon ΔE^*_{in} and ΔE^*_{out} from growth curves.

For other LDPE samples with $\bar{M}_w$ similar to that of Sclairfilm, the flow activation energy (calculated from the temperature dependence of the viscosity) is only about one-half ΔE^*_{in} or ΔE^*_{out}.[32] Insofar as flow activation is a measure of the energy to move intertwined (reptating) chain segments,[33] diffusion activation energies indicate that a process in addition to polymethylene segmental motion is required for DMA to permeate LDPE. Since our experiments monitor the entry and exit of DMA molecules to and from specific dopant sites (those occupied by a pyrenyl group), the additional energy may be related to difficulties in occupying those sites and in adopting ex-

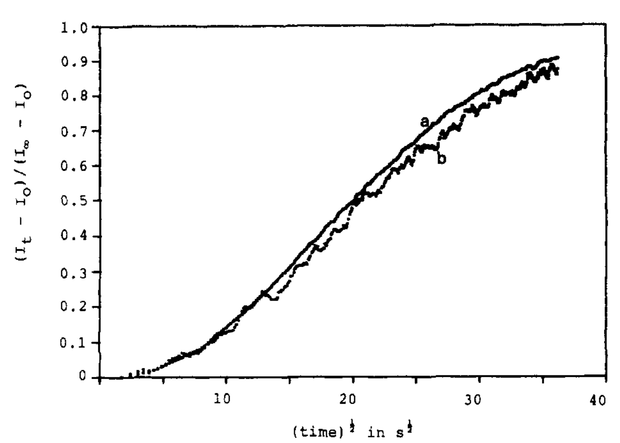

Figure 6. Plot of fluorescence intensity changes at 395 nm (λ_{ex} 343 nm) versus the one-half power of time for (a) unstretched and (b) stretched pyrenyl-LDPE films at 31 °C in methanol. The films were preequilibrated with 0.5 M DMA in methanol solutions.

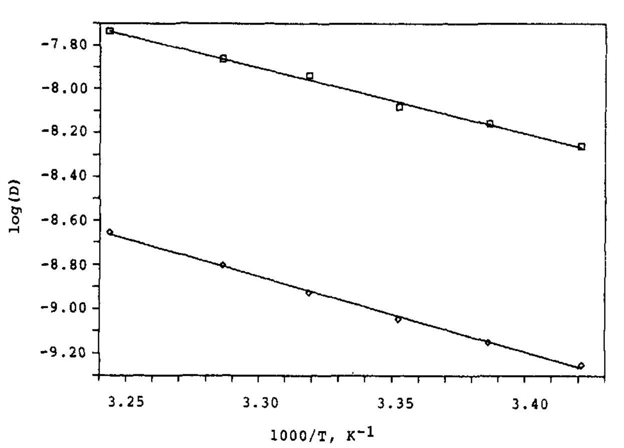

Figure 7. Arrhenius plots for DMA diffusion coefficients derived from fluorescence growth curves of unstretched (□) and stretched (◇) pyrenyl-LDPE films in methanol.

Table V
Diffusion Coefficients and Activation Energies of Diffusion Coefficients for DMA in Pyrenyl-LDPE Films

T (±0.5), °C	10^9D,[a] cm^2/s unstretched	10^9D,[a] cm^2/s stretched
19	5.5 ± 0.5	0.56 ± 0.08
22	7.0 ± 0.7	0.71 ± 0.01
25	8.3 ± 0.3	0.91 ± 0.03
28	11.5 ± 0.3	1.2 ± 0.1
31	13.8 ± 0.3	1.6 ± 0.1
35	18.4 ± 0.6	2.2 ± 0.1
E_d, kcal/mol	13.6 ± 0.5	15.6 ± 0.4

[a] Each D value from which the reported averages were calculated had a correlation coefficient ≥0.997 (unstretched) or ≥0.992 (stretched).

ciplex-like orientations (i.e., factors associated with free volume[34]). In this regard, we emphasize that our diffusion activation energies reflect processes occurring *only* at sites to which DMA diffuses somewhat slowly: sites that are occupied rapidly or are inaccessible due (presumably) to insufficient free volume, or a lack of an amorphous entry pathway for DMA, are not probed. The fraction of the latter sites increases dramatically when pyrenyl-LDPE films are stretched (see Figure 2).

Comparisons with Other Diffusion Data for LDPE. We are unaware of other studies that compare diffusion coefficients (D) or activation energies in unstretched and stretched LDPE. In fact, most of the methods to measure D[35-38] and activation energies[39] of dopant molecules in unstretched LDPE have employed indirect methods or required postdiffusion analyses.

The Ds for DMA in unstretched and stretched pyrenyl-LDPE were calculated from plots of fluorescence intensity versus the square root of time (at early time) according to eq 11 (that holds for Fickian diffusion in films).[40]

$$\frac{M_t}{M_\infty} = \frac{4}{l}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \tag{11}$$

The mass uptake of DMA diffusant at time = t and ∞ (M_t and M_∞, respectively) can be substituted by fluorescence intensities as shown in eq 12.

$$\frac{I_t - I_0}{I_\infty - I_0} = \frac{4}{l}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \tag{12}$$

For reasons mentioned previously, we have more confidence in diffusion coefficients obtained with growth curve data and only they are reported. Representative plots of fluorescence intensity versus the one-half power of time for DMA diffusion in unstretched and stretched pyrenyl-LDPE are shown in Figure 6. D values were calculated from the slopes from the flat portion of rise (100–900 s for unstretched pyrenyl-LDPE at 31 °C), taking average values of the film thickness, l. The average D values from four different experiments ($[\mathrm{DMA}]_0$ = 0.5, 0.65, 0.80, and 0.95 M for the decay experiments that preceded the fluorescence rise data) at each temperature were plotted in Arrhenius form (Figure 7) to determine the activation energy associated with DMA diffusion coefficients (Table V).

Moisan has noted that the temperature dependence of diffusion coefficients for dopants in unstretched LDPE usually follows Arrhenius-like behavior.[41] The activation energies, E_d, so calculated for liquid dopants of similar size to DMA are near the values of $\Delta E^{\ddagger}_{in}$ and $\Delta E^{\ddagger}_{out}$ reported here. This correspondence gives us confidence that the activation energies measured by us using pyrenyl-LDPE and the E_d from Moisan[41] are related to the same phenomenon. As expected, our E_ds are also very similar to the $\Delta E^{\ddagger}_{in}$ and $\Delta E^{\ddagger}_{out}$ determined from k_{in} and k_{out};[41] their mechanistic interpretation follows correspondingly.

A similar determination of D for dopants in unstretched LDPE has been made by Wang and Howell.[37a] In their experiments, the fluorescence intensity of the *dopants* was measured as a function of time in the partitioning solvent, 1-propanol. Their value of D for 3-*tert*-butyl-4-hydroxyanisole at 31 °C, 3.8 × 10^{-9} cm^2 s^{-1},[37c] and the value for 2,6-di-*tert*-butyl-4-methylphenol at 30 °C, 2.9 × 10^{-10} cm^2 s^{-1}, obtained by Chang et al.[35] lend credance to our D value for DMA at 31 °C in unstretched pyrenyl-LDPE, 1.4 × 10^{-8} cm^2 s^{-1}. Both of the aforementioned molecules are larger than DMA and, therefore, are expected to exhibit somewhat lower D values.

As noted in Table V, the E_ds for DMA in unstretched LDPE are very similar to the values calculated in stretched LDPE. Although the slightly higher E_d in the stretched film may not be significant since the absolute error associated with these calculations is somewhat larger than for experiments in unstretched films, the differences in D values are worthy of note: as shown previously, the fraction of the total pyrenyl fluorescence quenched by DMA in stretched LDPE is much smaller than in unstretched. These differences are consistent with a slightly more protected environment around pyrenyl groups in stretched films.

Conclusions. We have demonstrated with low-density polyethylene the utility of a new method for the measurement of diffusion rates in real time, diffusion activation energies, diffusion coefficients, and the distribution of dopant sites. The experiments rely upon photochemically induced covalent attachment of a fluorescent molecule, pyrene, to the polymer chains. Comparison of data from unstretched and stretched polymer films that share a common history allows the microscopic consequences of macroscopic film stretching to be identified: on the average, dopant sites become smaller, but the activation energy for diffusion changes little, if at all.

The techniques described here should be applicable to a wide variety of polymers and dopant molecules. As analytical tools, the techniques may allow various formulations of one polymer type to be differentiated on the basis of dynamic properties that complement existing static measurements.

Acknowledgment. We thank Brian Blackedar and Ann Walski of Du Pont of Canada for the polyethylene used in this work and for information concerning its properties. Robert Fidler of Metter Instruments Corp. and Dr. Richard Treanor kindly performed the differential scanning calorimetry measurements. Dr. Michelle Lamotte is thanked for several enlightening discussions on the scientific uses of sandwich bags. We gratefully acknowledge the National Science Foundation (Grants CHE 85-17632 and CHE 88-18873) for its support of this work.

Appendix

A static model for DMA quenching of pyrenyl (P) singlets in unstretched and stretched films is presented in eq 13–18. The model is predicated upon several reasonable assumptions that must be at least approximately valid:

(1) Molecular motions of DMA molecules during the lifetime of a pyrenyl singlet play a very small role in the amount of quenching detected (i.e., DMA entry and exit rates from a bound dopant site are much slower than pyrenyl deexcitation rates).

(2) The probability of pyrenyl excitation depends upon neither the type of its dopant site nor the presence or absence of a neighboring DMA molecule.

(3) The rate constants for the individual processes in the equations do not change when a film is stretched.

(4) Sites containing both a pyrenyl group and a DMA yield no free pyrenyl fluorescence and form exciplexes quantitatively.

$$\mathrm{P} \xrightarrow{h\nu} {}^1\mathrm{P} \tag{13}$$

$$\overline{\mathrm{DMA} + \mathrm{P}} \xrightarrow{h\nu} {}^1(\mathrm{P}^{\bullet}\mathrm{DMA}) \tag{14}$$

$${}^1\mathrm{P} \xrightarrow{k_1} \mathrm{P} + h\nu' \tag{15}$$

$${}^1\mathrm{P} \xrightarrow{k_2} \mathrm{P} + \Delta \text{ or } {}^3\mathrm{P} \tag{16}$$

$${}^1(\mathrm{P}^{\bullet}\mathrm{DMA}) \xrightarrow{k_3} \overline{\mathrm{P} + \mathrm{DMA}} + h\nu'' \tag{17}$$

$${}^1(\mathrm{P}^{\bullet}\mathrm{DMA}) \xrightarrow{k_4} \overline{\mathrm{P} + \mathrm{DMA}} + \Delta \tag{18}$$

$$I_1^{\mathrm{MeOH}} = \beta I_a k_1/(k_1 + k_2) \tag{19}$$

In the absence of DMA, the intensity of pyrenyl emission, I_1^{MeOH}, is given by eq 19 where I_a is the intensity of absorbed light and β is the fraction of the total light emitted at the monitoring wavelength. In the presence of DMA, I_1^{MeOH} must be modified as shown in eq 20 to include two additional considerations: (1) only a fraction $(1 - \chi)$ of I_a is absorbed by DMA-free pyrenyl sites; (2) absorption by DMA at the excitation wavelength ($\mathrm{OD}_{343} \simeq 0.2$ for a 0.5-cm pathlength of 0.95 M DMA) causes I_a to be reduced. The value of α, which is related to the optical density of DMA, could not be determined accurately in our experiments since 343 nm is on a steep absorption shoulder of DMA.

$$I_1^{\mathrm{DMA}} = (1 - \chi)\alpha\beta I_a k_1/(k_1 + k_2) \tag{20}$$

In the same way, the exciplex emission intensity I_3 can be expressed by eq 21. Three mechanistically useful ratios (eq 22–24) derive from these expressions: when recorded under the same fluorimeter conditions, the emission intensities remove I_a as a variable.

$$I_3 = \chi\alpha\beta' I_a k_3/(k_3 + k_4) \tag{21}$$

$$I_3/I_1^{\mathrm{MeOH}} = \frac{\chi\alpha\beta' k_3/(k_3 + k_4)}{\beta k_1/(k_1 + k_2)} \tag{22}$$

$$I_3/I_1^{\mathrm{DMA}} = \frac{\beta'\chi k_3/(k_3 + k_4)}{\beta(1 - \chi)k_1/(k_1 + k_2)} \tag{23}$$

$$I_1^{\mathrm{DMA}}/I_1^{\mathrm{MeOH}} = \alpha(1 - \chi) \tag{24}$$

By ratioing the values for unstretched (u) and stretched (s) films, the last undetermined factors are eliminated (eq 1–3).

Registry No. DMA, 121-69-7.

Supplementary Material Available: Two tables of $k_{\mathrm{in}} + k_{\mathrm{out}}$ for DMA from pyrenyl-LDPE fluorescence decay and growth curves (2 pages). Ordering information is given on any current masthead page.

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Inclusional Association of Phenolphthalein with Cyclodextrins in the Presence of Polyelectrolytes and Ionic Detergents As Studied by the Temperature-Jump Technique

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Received January 12, 1989

ABSTRACT: The forward (k_f) and backward (k_b) rate constants and the association constants (K) of the inclusional association of phenolphthalein (PP) dye into the cavities of α- and β-cyclodextrins (CD) are determined using a temperature-jump technique in the presence of simple electrolytes, polyelectrolytes, and ionic detergents. The kinetic parameters are obtained very accurately using the substantial changes in the absorbance of PP in the course of the inclusion process. The apparent values of k_f and K decrease on the addition of hydrophobic macroions and detergents having long alkyl groups, whereas k_b increases. The driving forces of the inclusion process of PP or hydrophobic and cationic macroions with CD's are the van der Waals and hydrophobic interactions between the hydrophobic groups of the guest molecules and the inner wall of the cavity of the cyclodextrin.

Introduction

As is well-known, cyclodextrin (abbreviated as CD hereafter) is one of the most appropriate compounds to mimic enzymic systems.[1–5] This is because the cavity of a CD molecule can provide a hydrophobic environment for a guest molecule in an aqueous medium and can form complexes with a variety of molecular species. Among many guest molecules, dye molecules have been used for study of the inclusional associations, since the chromophoric changes accompanied with the association are really convenient for studying the static and dynamic properties. The inclusional association of phenolphthalein (PP), a typical indicator, with β-CD has been reported by Lautsch et al.[6] and recently by Taguchi.[7] Studying a kinetic analysis of the PP + CD systems has the advantage that the absorption peak of the dye disappears completely due to the inclusion as is shown below in Figure 1, and accurate determination of the kinetic and static parameters may be performed. Most of the dye molecules studied hitherto exhibited very small shifts in absorption peak by the inclusional association.

It has been reported that alkyl groups of ionic detergents and polyelectrolytes may be included in the cavities of CD's.[8–14] The following sections discuss in detail the

0024-9297/89/2222-3936$01.50/0