Insights into the Mechanism of Diffusion of Some *N,N*-Dialkylanilines in "Native" Low Density Polyethylene Films Using a Simple Fluorescence Technique†

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ABSTRACT: A simple, sensitive fluorescence method for following quantitatively the rates of diffusion of guest molecules in native polymer films is demonstrated using three *N,N*-dialkylanilines (DAA; alkyl = methyl, ethyl, and *n*-butyl) as guests and low density polyethylene (LDPE) as the polymer. Both Fickian and first-order rate models are used. The results are compared with those obtained previously using LDPE films with fluorophores attached covalently to interior chains. They indicate that diffusion occurs as a distribution of event types whose ensemble average is being measured. The very high and similar diffusional activation energies calculated for the three DAA in LDPE are consistent with a microscopic model in which polymethylene chain motions in addition to those experienced normally by the polymer are required to move the guest molecules. It is suggested that synchronous motions of at least two vicinal chains may be necessary.

Introduction

Recently, we have reported[1-6] several new methods which allow the following to be determined: (1) the free volume distribution of sites occupied by guest molecules in polymer matrices; (2) the rates of diffusion to and from those sites, measured in *real time*; (3) the shape and free volume changes which occur at the sites as the polymer films are stretched. Demonstrations of feasibility have been conducted on unstretched and stretched films of low density polyethylene (LDPE) which are modified at internal sites with covalently attached 1-pyrenyl[1] or (9-anthryl)methyl[2] reporter groups. Since the modified films provide only information on events at or emanating from the sites with reporter groups, we have endeavored to complement those results with experiments employing native films. A preliminary account of such efforts, allowing the diffusion coefficients of anisole in LDPE to be measured, has appeared.[4] Here, we demonstrate in greater detail and with three homologous *N,N*-dialkylanilines (DAA) [*N,N*-dimethylaniline (DMA), *N,N*-diethylaniline (DEA), and *N,N*-di-*n*-butylaniline (DBA)] as diffusants the conditions under which the technique may be employed. Those conditions are sufficiently unrestrictive so that the technique should allow the diffusion of a large number of guest molecules in a wide variety of polymer films to be measured quantitatively and in real time with excellent sensitivity.

Comparison of results obtained in this way with the native films and with those reported previously using modified films allows additional conclusions concerning the micromorphology of the polymers to be deduced.

Technique

Initially, an LDPE film (mounted on a glass yoke to keep it taut)[1,7] is doped with a low concentration of DAA. When the film is immersed in an N_2-saturated solution of 2 N HCl, the DAA molecules begin to equilibrate between the film and the liquid. Excitation of DAA molecules within the film leads to fluorescence; fluorescence of DAA in the aqueous portion is attenuated severely due to quenching of the excited singlet states by aqueous acid, to decreased molar extinction coefficients at the excitation wavelength (Scheme 1; Figure 1), and to high dilution of DAA in the beam of excitation radiation. DAA molecules which escape a film are dispersed throughout the liquid into the regions where the excitation beam does not pass. Since water and HCl molecules do not enter the polymer to an appreciable extent, the change in intensity of the fluorescence at one excitation wavelength and one emission wavelength as a function of time provides a history of the partitioning. The volumes of the film and the liquid in the sample and the magnitude of the partitioning coefficient for DAA between them ensure that virtually all of the DAA will reside in the aqueous liquid at equilibrium. A more detailed description of the procedures employed is included in the Experimental Section.

Clearly, the same approach can be used with many different polymer films which do not absorb at wavelengths where their potentially fluorescent guest molecules can be excited electronically and with many different liquids which contain polymer-insoluble contact quenchers of the guest fluorescence.

Experimental Section

Low-density polyethylene films (Sclairfilm 300 LT-1; 76 μm thick; 0.92 g/cm^3; M_w = 112 600[8]) were supplied by DuPont of Canada. On that basis, they are about 50% amorphous and 50% crystalline. Prior to being doped with a DAA, films were immersed in a large volume of chloroform (ACS grade) for 1 day to remove plasticizers and antioxidants. The DAA, gifts from Drs. Roseann Jenkins and Zhiqiang He, were >99% pure according to glpc analyses. They were stored under nitrogen and refrigerated until use. The 2 N HCl solutions were prepared freshly from distilled water and concentrated (10 N) HCl (Fisher ACS grade). Methanol from which doping solutions were prepared was ACS grade also.

As described previously, films were attached to a glass yoke.[1] They were immersed in methanolic solutions of (1–2) × 10^{-2} M DAA for predetermined periods which allow 10^{-3} to 10^{-5} M DAA to be imbibed into the films. Upon removal from the bath, the films were washed quickly with a small quantity of methanol to remove any DAA on the surfaces and dried in the air for 1–2 min. They were placed immediately into a quartz cuvette containing 3 mL of 2 N HCl which had been temperature equilibrated (±0.5 °C) in the cell compartment of a SPEX 111 Fluorolog fluorometer equipped with an Osram 150 W/XBO high-pressure Xe lamp and an IBM compatible computer. The slits were fixed throughout at 1.25, 0.5, 0.5, and 0.5 mm from the lamp to the detector. Temperature was monitored using a calibrated thermister that was in contact with the cuvette. The intensity of fluorescence

† Dedicated to Dr. Arnold R. Brossi on the occasion of his 70th birthday.

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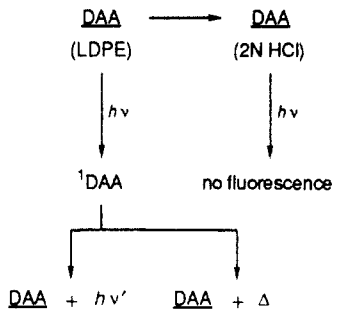
Scheme 1



at 350 nm (λ_{ex} = 300 nm) was measured either in front-face or right-angle configurations until the change with time was imperceptably small. Once a run was started, the film and cuvette were not moved in order to avoid sudden intensity changes. Films were used repeatedly; all of the reported data were obtained on three pieces of the LDPE. Data were collected and analyzed with a Basic program written by Mr. Bill Craig.

Concentrations of DAA in the films were determined for various periods of doping as described previously.[1] Essentially, DAA in a film was extracted into 3 mL of methanol and the concentration in the methanol was calculated using Beer's law and the molar extinction coefficients at 262 nm (1.5×10^4 for DEA and 3.4×10^4 for DBA) or 254 nm (1.3×10^4 for DMA), the absorption maxima. Since the density, weight, and thickness of each film strip were known, the concentration of DAA in the methanol can be related directly to the concentration initially in the film.[1,2]

Results

Steady State Emission and Excitation Spectra. The emission and excitation spectra of the DAA were recorded in several solvents. All provided unstructured fluorescence bands in both water and hexane. The extrema of the emission and excitation spectra are collected in Table 1. Representative curves for DMA are presented in Figure 1. In 2 N HCl, the small magnitudes of the molar extinction coefficients at the excitation coefficients at the excitation wavelength and acid quenching make the fluorescence of comparable concentrations of DAA very difficult to observe. Comparison between the absorption characteristics for DMA in water and 2 N HCl (Table 1) shows that almost all of the DAA in the latter are protonated in their ground states.

In LDPE films, the DAA can be excited conveniently at wavelengths where the host matrix does not absorb. However, due to morphological inhomogeneities at the surfaces of and within the films, the intensity of detected emission varies dramatically at different positions on the film surface. While recording steady-state emission spectra or time-dependent intensity changes from DAA in a film, care was taken not to move the cuvette or the yoke holding a film.

Time-Dependent Emission Spectra. We have attempted to measure emission decays like that shown in Figure 2 from as close to the moment when the DAA-doped film is placed in the aqueous bath as is possible. Practically, the physical manipulations associated with introducing the various components to each other require at least 30 s. In some of the data manipulations, especially those using an integrated form of Fick's second law for diffusion at "early" times (eq 1),[9,10] we have extrapolated

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

the intensity curves to the estimated time = 0 values and used them in subsequent work. Failure to do so introduces

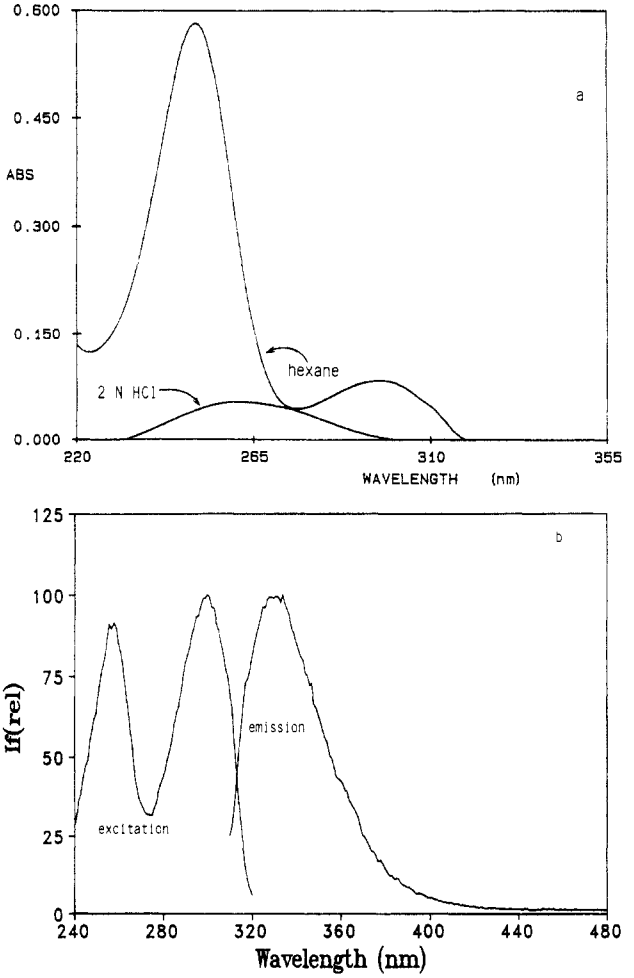


Figure 1. (a) Absorption spectra of DMA in hexane and in 2 N HCl and (b) emission (λ_{ex} = 300 nm) and excitation (λ_{em} = 350 nm) spectra of 4×10^{-5} M DMA in N_2-saturated hexane. Emission and excitation spectra of 4×10^{-5} M DMA in 2 N HCl were almost imperceptible under the conditions above.

Table 1. UV/Vis Absorption and Emission Characteristics of DAA in Various Solvents at Room Temperature

			absorption		emission	
DAA	conc, M	solvent	λ_{max}, nm	ϵ_{max}	λ_{em}, nm[a]	λ_{ex}, nm[b]
DMA	1.3×10^{-4}	hexane	290	2.0×10^3	330	265, 300
			250	1.5×10^4		
	1.3×10^{-4}	water	295 (tail)	1.4×10^3	360	260, 295
			245	9.1×10^3		
	1.3×10^{-4}	2 N HCl	260	1.3×10^3	(330)[c]	(300)[c]
	1.1×10^{-4}	methanol	300	2×10^3	350	260, 302
			254	1.3×10^4		
DEA	4.2×10^{-5}	methanol	306	2.0×10^3	344	260, 302
			262	1.5×10^4	344	260, 302
DBA	5.0×10^{-5}	methanol	306	2.4×10^3	354	263, 307
			262	1.8×10^4		

[a] λ_{ex} = 300 nm. [b] λ_{em} = 350 nm. [c] Very weak intensity.

small (<5%) differences in the values of the calculated diffusion constants. I_0, I_t, and I_∞ are the fluorescence intensities at, respectively, time = 0, t, and ∞, D is the diffusion coefficient of DAA in LDPE, and l is the thickness of the film. I_∞ is taken to be when the fluorescence intensity changes by less than 1% of its intermediate value during a 30-min period.

Since the *rate* of diffusion of DAA *into* a film during an experiment is negligible in comparison with the rate of diffusion out of the film, decays like those in Figure 2 can also be treated as first-order kinetic processes according to eq 2. The resulting graphs, generated by application of

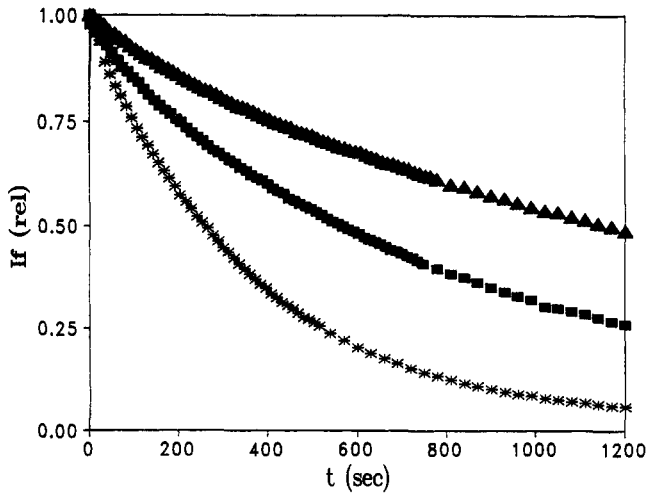


Figure 2. Fluorescence decay (out-diffusion) curves from an LDPE film doped with DMA and in contact with 2 N HCl at 15.0 (▲), 25.5 (■), and 34.0 °C (*).

$$\ln\left[\frac{I_t - I_\infty}{I_0 - I_\infty}\right] = -kT \qquad (2)$$

eqs 1 and 2 to the decay curves, are exemplified by Figures 3 and 4. The straight lines are linear least-squares fits to the 0.5–0.8 ordinate portion of the data in Figure 3 or to all of the data after the initial 200 s (*vide infra*) in Figure 4. In all cases except for DMA at 15 °C, the D were determined from data in the 0.4–0.8 range along the ordinate. The D or rate constant (k) values so calculated from different runs using the same film or from different films usually deviated by no more than 10%. The averages from several runs at various temperatures, where the morphology of the LDPE should be virtually constant,[7,11] are reported in Table 2. Correlation coefficients (r) for data fits to calculate D or k in individual runs were excellent, usually ≥0.99 and never <0.98.

In fact, $k = D\pi^2/l^2$ since eq 2 has the same form as the first term of the infinite series which expresses Fickian diffusion in a film.[9c] Both the values of k calculated from D and from eq 2 are included in Table 2. They are in reasonable agreement, as they should be if the assumptions for our diffusion model (*vide infra*) are approximately correct.

Using Arrhenius-type treatments (eqs 3 and 4),the D

$$D = D_0 e^{-E_D/RT} \qquad (3)$$

$$k = k_0 e^{-E_k/RT} \qquad (4)$$

and k values allow the associated activation energies (E_D[12] and E_k) for diffusion of the DAA to be calculated (Table 3 and Figures 5 and 6). The pre-exponential values, D_0 and k_0, are not reported since they must be extrapolated from a relatively small temperature range and may be very inaccurate.

The differences in the diffusive properties of the DAA in the LDPE films were qualitatively discernible by the times required for the I_∞ values to be reached at one temperature. At 25 °C, these times correspond to approximately 2 h for DMA, 3.5 h for DEA, and 6.5 h for DBA. The increased times for the larger DAA are consistent with the respective D and k values, but do not correlate with the activation energies in Table 3 which are related to the temperature dependence on diffusion.

The influence of the initial concentration of DAA in the films on the dynamics of diffusion has been examined somewhat. After being submerged in 1.8×10^{-2} M DMA or DBA in methanol for periods which varied from 1 to 12 h, the doped films were found to yield k values at 31

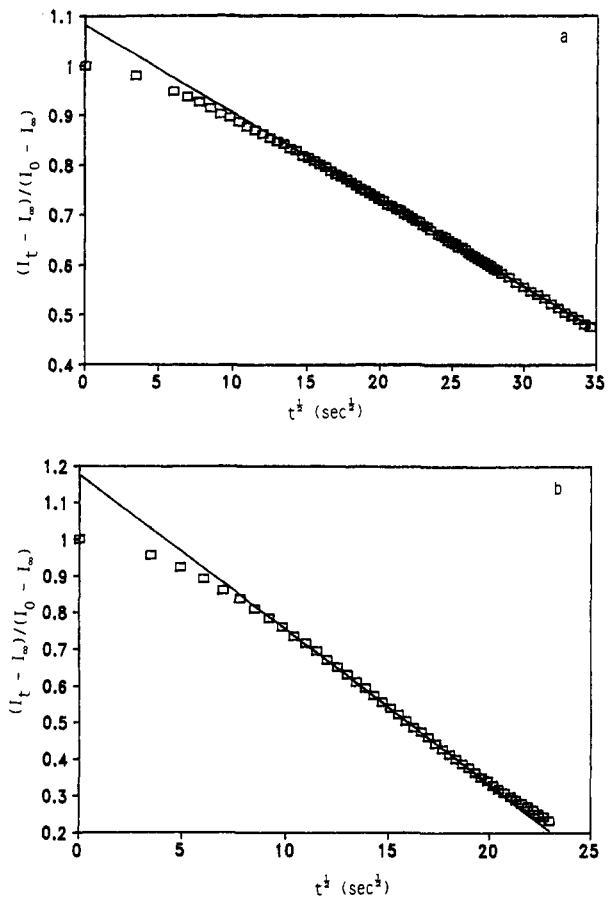


Figure 3. Treatment of data in Figure 2 according to eq 1 at 15 °C (a) and 34 °C (b).

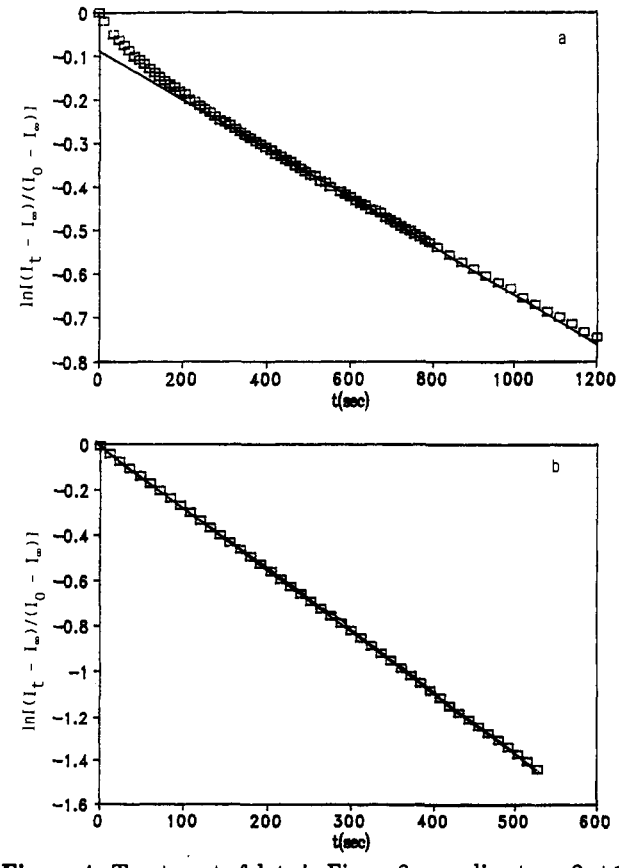


Figure 4. Treatment of data in Figure 2 according to eq 2 at 15 °C (a) and 34 °C (b).

Table 2. Diffusion Coefficients and Rate Constants for DAA Out-Diffusion from LDPE Films[a]

DAA	T °C	10^8D, cm²/s	10^4k,/s	10^4k,[b] s⁻¹
DMA	15	0.40 ± 0.03	5.7 ± 0.2	6.8 ± 0.5
	20	0.51 ± 0.04	8.1 ± 0.2	8.7 ± 0.7
	25.5	0.90 ± 0.02	12.3 ± 0.1	15.4 ± 0.3
	29	1.20 ± 0.06	17.2 ± 0.6	20.5 ± 1.0
	34	1.98 ± 0.12	27.5 ± 1.2	33.8 ± 2.0
DEA	20	0.17 ± 0.01	3.0 ± 0.2	2.9 ± 0.2
	24	0.22 ± 0.03	3.8 ± 0.4	3.8 ± 0.5
	27	0.31 ± 0.02	5.0 ± 0.1	5.3 ± 0.3
	30	0.38 ± 0.02	6.4 ± 0.1	6.4 ± 0.3
	34	0.53 ± 0.03	8.8 ± 1.2	9.1 ± 0.5
	39	0.83 ± 0.04	13.7 ± 1.2	14.2 ± 0.7
DBA	24.5	0.14 ± 0.02	2.3 ± 0.1	2.4 ± 0.3
	29.5	0.21 ± 0.01	3.0 ± 0.2	3.6 ± 0.2
	33	0.23 ± 0.02	3.5 ± 0.3	3.9 ± 0.4
	38	0.39 ± 0.03	6.0 ± 0.3	6.7 ± 0.3
	43	0.54 ± 0.06	8.9 ± 0.6	9.2 ± 0.8

[a] Each entry represents an average of at least 3 separate runs. See text for further details. [b] Calculated from $k = \pi^2D/l^2$ using the D values in the table.

Table 3. Activation Energies for DAA Out-Diffusion from LDPE into 2 N HCl or from LDPE with Covalently Attached 1-Pyrenyl Groups into Methanol

DAA	E_D, kcal/mol		E_k, kcal/mol	
DMA	15.1 ± 0.3	(13.6 ± 0.5[a])	14.5 ± 0.1	(12.7 ± 0.5[a]) (13.0[b])
DEA	15.2 ± 0.4		14.7 ± 0.1	(9.2 ± 0.4[b])
DBA	13.4 ± 0.2		13.7 ± 0.1	(6.0 ± 0.8[b])

[a] Pyrenyl-substituted LDPE.[1] [b] Pyrenyl-substituted LDPE.[3]

°C which are consistent within the limits of our experimental error. This result is not surprising since the total concentration of DAA in all cases remains very low, $\leq 7 \times 10^{-3}$ M or about double the 1-h value after 2 h of soaking, and should not swell the films perceptably.

Discussion

The methods currently available to follow the diffusion of small molecules in polymers include sorption or desorption,[13] pulse-gradient spin-echo NMR,[14] radio tracers,[15] fluorescence intensity of nonswelling liquids in contact with doped polymers,[16] and gas chromatography.[17] Each requires elaborate equipment and sample preparation, difficult to handle or prepare chemicals, or relatively high concentrations of diffusing molecules in the polymer. Our recent efforts to develop simpler, more sensitive real-time methods for the measurement of diffusion by small molecules in polymers have included covalent attachment of fluorophores to the interiors of films and monitoring of the temporal changes in the fluorescence intensity which occur as a small quencher is allowed to diffuse into or out from the film. Where comparisons with existing data have been possible,[15d,16] the diffusion coefficients calculated using this method are very close to the values obtained from experiments using the more classical methods.

In spite of the success of the fluorescence techniques, we recognize that they have limitations and may not always lead to data which are reflective of bulk diffusion. For instance, not all of the polymer films we wish to investigate can be derivatized by our techniques; the alternative, copolymerization methods, is unsatisfactory since it incorporates fluorophores at both the surface and the interior of a film, and the nature of the sites at which they reside is determined in large part by the fluorophore groups themselves, rather than the morphology of the unadulterated polymer. Also, the sites at which derivatization does occur using our methods are limited by the amount of free volume accessible to the precursor reagents

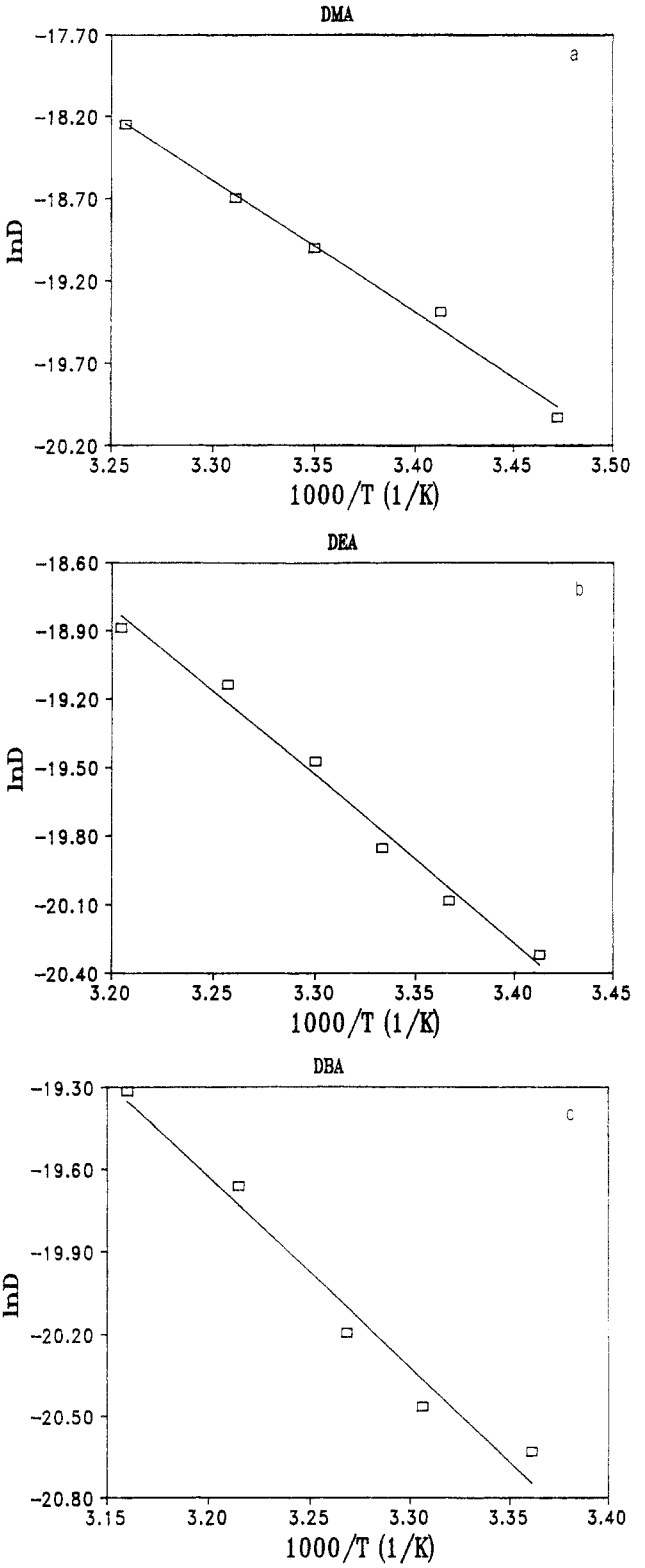


Figure 5. Arrhenius plots for out-diffusion of DAA from LDPE using diffusion coefficients: (a) DMA; (b) DEA; (c) DBA.

within the polymer; some sites may be inaccessible to the reagents because of restrictions in the pathways to them, others may be intrinsically too small to permit a reagent to enter, and still others may lack adequate free volume to permit the entry of both a covalently-attached fluorophore and a quencher molecule. Although we have presented arguments which indicate that entry of the first quencher molecule into a fluorophore-modified site (for in-diffusion) or exit of the last quencher molecule from it (for out-diffusion) is not the rate-limiting diffusional step in LDPE films, there is no assurance that it may not be

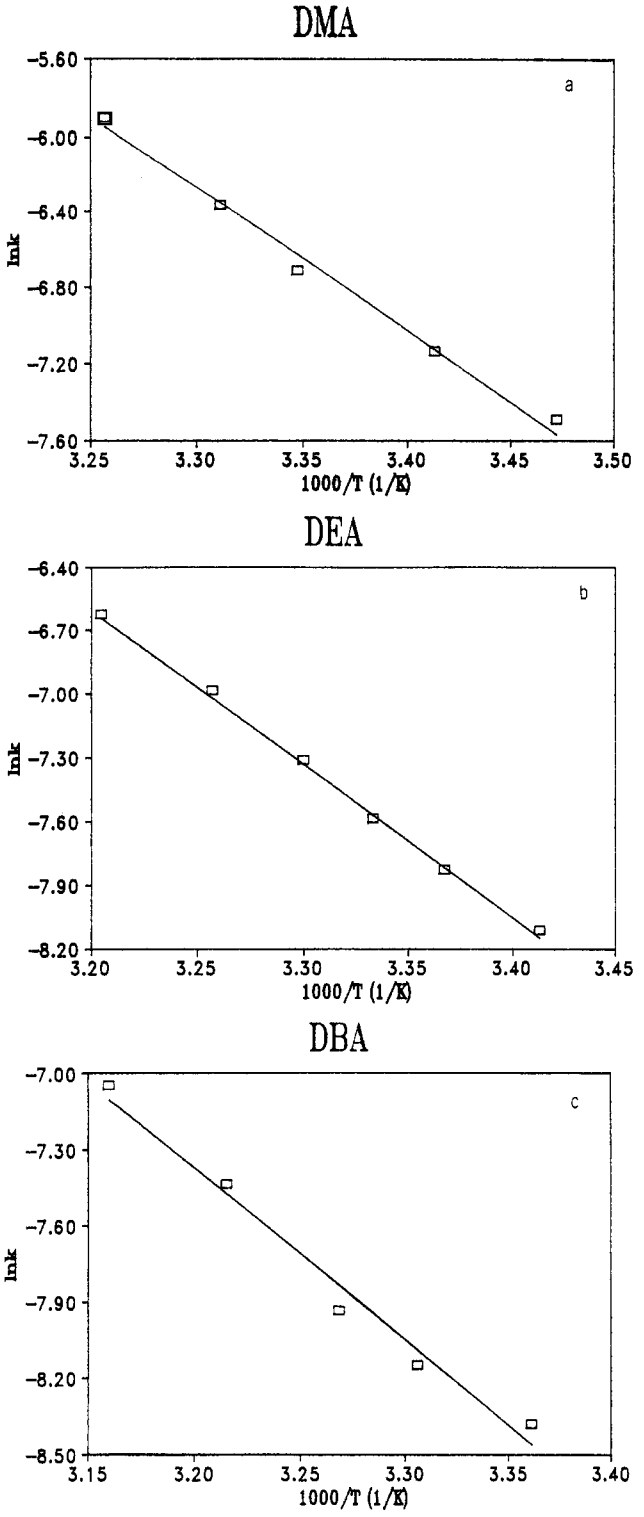


Figure 6. Arrhenius plots for out-diffusion of DAA from LDPE using rate constants: (a) DMA; (b) DEA; (c) DBA.

in others. Thus, the diffusion coefficients may not reflect accurately the total population of the diffusant since only those quenching molecules able to reach a covalently-attached fluorophore can be detected by the fluorescence intensity changes. Evidence for such complications and for a distribution of site types has been found in previous studies employing LDPE films and 1-pyrenyl or (9-anthryl)methyl as the covalently-attached fluorophore group.[1-3]

More recently, we have demonstrated that it is possible to dispense with a covalently-attached fluorophore and use native films.[4] The system chosen as a test was anisole in LDPE films. A major advantage of this method is that it allows *all* of the diffusing molecules to be accounted for in the diffusion measurements. To demonstrate further the applicability of the method and to compare results from it with those from our covalently-attached films, we have examined the diffusion of three DAA in LDPE.

The experimental nature of this approach limits detection, normally, to net diffusion out of the films. With the derivatized films, diffusion both into and out of the films could be followed. Although the two should result in equivalent diffusion coefficients and rate constants, they do not, in fact, because the immersing liquids are somewhat different. Arguments which support out-diffusion as being reflective of the movements of guest molecules in a more nearly undisturbed film environment rather than in-diffusion have been presented.[1] In this discussion, comparisons will be limited as much as possible to diffusional parameters obtained from other experimental techniques which involve out-diffusion. Previously, we have shown that movement of guest molecules within a film, and not their transfer across the interface between the film and the receiving liquid, is the rate-limiting diffusional process being measured in modified and native films.[2,4]

Within the temperature range investigated, significantly above the glass transition temperature and well below the melting temperature of the crystalline part of LDPE,[11,18] all of the fluorescence decay curves for the DAA could be fit to a single exponential function with good precision after ca. 1–3 min of detection. For this reason, calculation of k values using eq 2 was limited to data collected after 200 s. In other studies, we have detected small contributions from a second, faster decay component like the one presented here.[1] It may be related to β relaxation[11b] (associated with the movement of short branches located on chains in the amorphous region[19]), to diffusion of molecules from sites near the film surface, to a lack of complete temperature equilibration initially, to molecules escaping from especially porous sites, to film inhomogeneities, or to a combination of these factors. Alternatively, it may be a consequence of the expected multiexponential character of Fickian diffusion.[9c] In fact, we have attempted to avoid temperature domains where transitions associated with relaxation processes occur[11] in order to focus on comparisons with our earlier results. Atvars et al.[20] have shown that very useful information can be gleaned from spectroscopic measurements taken on luminescent probes in LDPE films over temperature ranges which include relaxation transitions. Our future work will explore these regimes.

A more precise "all-time" solution to a Fickian diffusion process in a film, which is morphologically homogeneous and contains an initial even distribution of dopant molecules, is given by eq 5.[9c] Figure 7 shows some solutions

$$\frac{I_t - I_\infty}{I_0 - I_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} e^{-[D(2n+1)^2\pi^2 t/l^2]} \qquad (5)$$

to eq 5 for different values of D when the infinite series is truncated to its first eight terms. Superimposed upon these are a representative data set from DMA diffusion at 25.5 °C. Although the experimental points do not fall on any of the calculated lines, they can be made to do so quite well by attempting to correct for the fact that the data set lacks the first few seconds of diffusion. Although this empirical manipulation may be of questionable validity, the best fit is clearly to a value of D of 6.5×10^{-9} cm^2/s, which is extremely close to that calculated from the simpler "early time" equation (1). On this basis, we have chosen to use primarily the simpler data treatment.

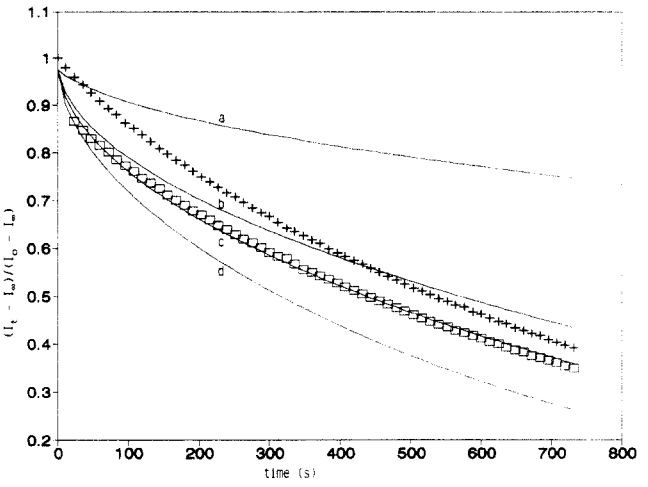


Figure 7. Representative plot of fluorescence intensity decay curves predicted by eq 5 using the first eight terms of the infinite series and $D = 10^{-9}$ (a), 5×10^{-9} (b), 6.5×10^{-9} (c), and 9×10^{-9} cm^2/s (d). Superimposed is a data set from diffusion of DMA at 25.5 °C (+) and the same data with each point divided by a constant (1.15) and offset by 24 s (□).

The values of D and k collected in Table 2 compare favorably with those obtained using An-LDPE and Py-LDPE films. However, systematic deviations do exist and they are most evident in comparisons with E_k calculated from DAA out-diffusion in Py-LDPE films (Table 3). Whereas the activation energies for diffusion of the DAA in the native film remain almost unchanged as the van der Waals volume of the homologue changes from 128.7 (DMA) to 162.8 (DEA) to 231.0 Å^3 (DBA),[21] they suffer a ca. 50% decrease when Py-LDPE is the film employed.[3]

The source of this discrepancy can be traced to factors alluded to previously. In the distribution of sites occupied by covalently attached pyrenyl (or anthryl) groups, only a fraction will possess sufficient *additional* free volume to allow at least one DAA molecule to reside therein also. *Only* these sites will be included in measurements of diffusion properties when the pyrenyl fluorescence intensity is being monitored. Since the fraction of those sites will decrease as the volume of the DAA molecules increases, the D and k values will always be prejudiced toward the comportment of molecules in the larger sites. If the access to and from those sites is also easier than the access to the smaller sites, it is obvious why the dynamic properties of the diffusing molecules will not be the same when measured by the two methods (i.e., in native and fluorophore-modified films).

In fact, we have demonstrated that the fraction of modified sites in unstretched Py-LDPE being accessed by DAA molecules decreases linearly with the *total* DAA concentration in a film as the size of the DAA increases: at equivalent doping concentrations, the equilibrium concentration of DMA in a film is twice that of DBA; the intensity decrease in pyrenyl fluorescence due to the DMA is twice that due to DBA.[3] Thus, the discrepancy between values for diffusion which take into account all DAA molecules and those which include only a selected fraction of them is expected to increase as the fraction decreases, and it does.

The magnitudes of the E_D for the DAA in the native LDPE are rather large. The flow activation energy (calculated from the temperature dependence of the viscosity) for an LDPE with M_w similar to that of Sclairfilm is only about half of the E_D.[22] Insofar as flow activation is a measure of the energy to move intertwined (reptating) polymethylene chain segments,[23] the E_D values indicate that migration of DAA molecules within a film requires extraordinary chain motions[20] by the local host. Even the highest energy (α) relaxation processes in LDPE have energies which are no more than ca. 10 kcal/mol.[11b] Thus, movement of the DAA within LDPE involves processes not common to the native (undoped) film. Since the width of an aromatic ring of a DAA molecule is nearly twice the diameter of a methylene chain, it is reasonable to suppose that guest motion requires the synchronous relaxation of at least *two* vicinal polymethylene chain segments. Alternatively (but less likely), the chain motions associated with bulk relaxation modes do not emanate from the regions where the guest molecules reside (N.B., the amorphous regions and the interfaces between crystalline lamellae and amorphous domains;[24] the crystalline domains, themselves, are not entered by guest molecules at the temperatures of our experiments[25]).

Regardless of which scenario is correct, it is clear that activation energies for diffusion should not be viewed as the result of motions across single, well-defined barriers. Clearly, the DAA molecules are confronted with a distribution of sites in LDPE films. These sites differ in their abilities to accept a guest molecule of fixed volume and shape and in the ease with which those guests can migrate to and from them. Within the two major site types, there must be subgroups which are more or less accessible than others. In essence, the diffusional rate parameters and associated activation energies being measured are the ensemble averages of many stochastic events. They are changed when the distribution of the events being followed is altered by the population of the diffusing species; the ease with which LDPE chain segments can reptate to allow the passage of a DAA molecule from an interior film site to the interface with the aqueous receiving liquid will determine the ensemble average for the diffusion.[3]

Conclusions

We have demonstrated how relatively simple, real-time fluorescence techniques may be applied to determine the diffusional characteristics of guest molecules in native polymer films. The techniques are very sensitive and can follow the diffusion of very low concentrations of guest molecules. They complement the methods developed by Wang *et al.*[16] which monitor the concentration of molecules in a receiving liquid but require higher initial concentrations of diffusing species in a film. Although the present example employs LDPE and dialkylanilines, the methods should be applicable to a wide variety of polymers and low molecular weight guest molecules.

Additionally, the present results provide insights into the factors which influence the ease of diffusion in polymers. In combination with results obtained using modified LDPE films, the present results demonstrate that there is a rather diverse distribution of site types for guest molecules. The extent to which each type is occupied determines the bulk diffusional properties. When diffusion from all occupied sites is being followed, as in the case of the DAA homologues (whose van der Waals volumes differ by more than 100 Å^3) in native LDPE, polymethylene chain motions are able, in a bulk sense, to distinguish the smallest from the largest molecule, but the temperature dependence on diffusion seems to be more a function of the polymer than the size of the molecules diffusing in it. As in the case with stretched LDPE films, we expect that there is a limit beyond which the polymer matrix of the unstretched native films will exhibit activation energies for diffusion which are acutely sensitive to guest sizes.

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