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A Simple, Sensitive Method To Measure Diffusion Coefficients of Fluorescing Molecules in Polymer Films. Anisole Diffusion in Low-Density Polyethylene

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Virtually all of the methods available currently to follow the diffusion of small molecules in polymer films or blocks (e.g., sorption or desorption,[1,2] pulse-gradient spin-echo NMR,[3] radiotracers,[4] fluorescence intensity of nonswelling liquids in contact with doped polymers,[5] and gas chromatography[6]) require elaborate equipment, difficult to handle or prepare chemicals, or high concentrations of the diffusing molecule in the polymer. In an attempt to overcome some of these difficulties and complications, we have developed some new approaches to determine diffusion rates of solute molecules based upon the fluorescence quenching of covalently attached fluorophores in low-density polyethylene (LDPE) films.[7-9] However, they still require slight alterations of the constitution of the polymer and yield precise diffusion rates only when the permeability of the mobile molecule in the polymer is relatively large.

Here, we report an extremely simple fluorescence method for the rapid and routine measurement of diffusion coefficients in polymer films and demonstrate its application with anisole as the diffusing molecule and LDPE (Sclair from Du Pont of Canada) as the polymer medium. The method is extremely sensitive (requiring very low concentrations of anisole) and can be performed without chemical modification of the polyethylene.

Initially, an LDPE film (mounted on a glass yoke to keep it taut[7]) is doped with a low concentration of anisole.[10] When the doped film is immersed in an N_2-saturated 3/2 (v/v) ethanol/water solution containing 0.5 M KI (a heavy-atom quencher[11]), the anisole molecules begin to equilibrate between the polymer and the liquid. Since the liquid and iodide ions cannot enter the film, anisole molecules remaining there can fluoresce efficiently. The experiments are conducted in a closed 1-cm quartz cuvette held in the thermostated cell compartment of our fluorimeter. Thus, the fluorescence intensity (I_t) of the film is monitored as a function of time to produce decay curves like those shown in Figure 1.

Anisole molecules which escape the film do not fluorescence since they encounter the iodide ions[11] and are dispersed throughout the liquid into regions where the excitation beam does not pass. Eventually, almost all of the anisole passes from the film to the aqueous ethanol due to the volume of the liquid being >100 times that of the film (i.e., $I_\infty \simeq 0$).

The diffusion coefficients (*D*) of anisole are calculated from the data in Figure 1a using Fick's second law.[12] The mass of anisole in the aqueous methanol at time = *t* and in the film at time = 0 ($(\text{anisole})^t_{\text{AQ}}$ and $(\text{anisole})^0_{\text{LDPE}}$, respectively; both expressed as numbers of molecules) can be equated to the fluorescence intensities as shown in eq 1 (where I_0 and I_∞ are the fluorescence intensities at time = 0 and at equilibrium, respectively). Since the mass uptake of anisole in aqueous methanol is the same as the loss in the LDPE film, the fluorescence intensity ratio can be used to calculate *D* as shown in eq 2. The value of *D* was calculated from the slope of a best linear fit of the interval in the curve, $0.20 \le (I_0 - I_t)/(I_0 - I_\infty) \le 0.65$.

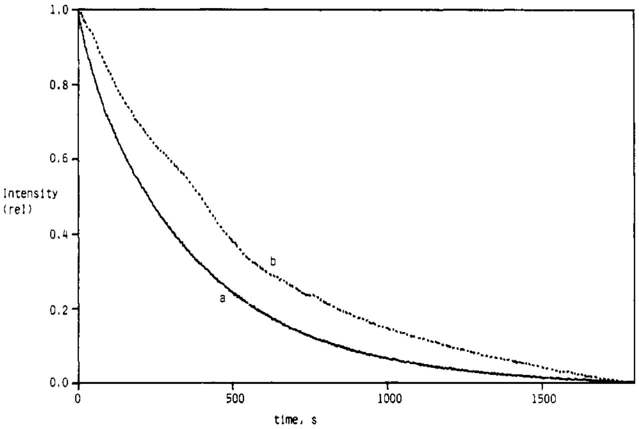

Figure 1. Fluorescence decay curves from anisole in an unstretched LDPE film. Receiving liquids are N_2-saturated 3/2 (v/v) ethanol/water with (a) and without (b) 0.5 M KI.

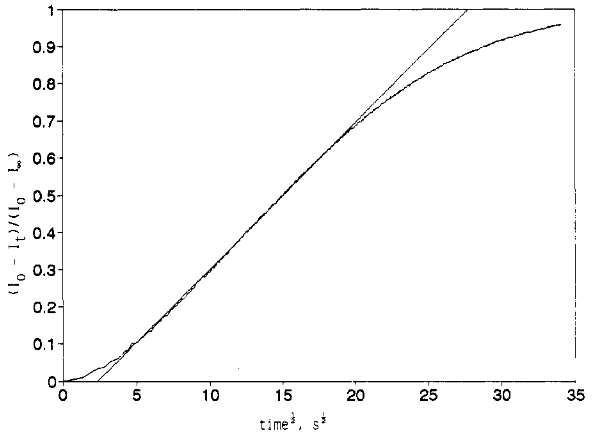

Figure 2. Fick's law plot of data in Figure 1a. The best linear fit of data along the ordinate between 0.2 and 0.65 is displayed, also.

$$(\text{anisole})^t_{\text{AQ}}/(\text{anisole})^0_{\text{LDPE}} = (I_0 - I_t)/(I_0 - I_\infty) \qquad (1)$$

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

Diffusion coefficients of anisole in unstretched and cold stretched (5×) LDPE films at 25 °C are reported in Table I. Anisole partition coefficients, measured between ethanol and LDPE at $[\text{anisole}]_{\text{EtOH}} = 1.9 \times 10^{-2}$ M,[7] were used to determine the equilibrium concentration of anisole in LDPE when $[\text{anisole}]_{\text{EtOH}} = 7.4 \times 10^{-4}$ M. The sensitivity of the present method is demonstrated by our ability to calculate *D* values for anisole with excellent precision when $[\text{anisole}]^0_{\text{LDPE}}$ is only 6.4×10^{-5} M. The errors cited are deviations from the statistical average of several runs. Our precision error is probably twice as large. Although we do not know, as yet, the lowest $[\text{anisole}]^0_{\text{LDPE}}$ concentration whose diffusion can be followed by our fluorimeter, the method is already more sensitive than others which employ fluorescence.[5,7-9]

The values of *D* reported in Table I for anisole are similar in magnitude to those calculated by other methods for

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Table I
Diffusion Coefficients for Anisole in LDPE at 25 °C and Associated Data

LDPE film	doping concn:[10] $[\text{anisole}]_{\text{EtOH}}$, M	film concn: $[\text{anisole}]_{\text{LDPE}}$, M	$D \times 10^8$,[c] cm^2/s
unstretched[a]	1.9×10^{-2}	1.6×10^{-3}	1.9 ± 0.1
	7.4×10^{-4}	6.4×10^{-5} [b]	1.6 ± 0.1
	1.9×10^{-2}	1.6×10^{-3}	1.8 ± 0.1[d]
stretched (5×)[a]	1.9×10^{-2}	1.1×10^{-3}	0.33 ± 0.03

[a] Film thickness is 76 μm before stretching and calculated to be 30 μm after stretching (assuming constant density). [b] Calculated from the partition coefficient measured when $[\text{anisole}]_{\text{EtOH}} = 1.9 \times 10^{-2}$ M. [c] Error limits are deviations from the statistical average of ≥3 separate determinations. [d] Quenching medium also contains 1 M KOH.

molecules of comparable size and shape in unstretched LDPE at 25 °C: $D = 1.977 \times 10^{-8}$ (benzene), 1.813×10^{-8} (toluene), and 1.567×10^{-8} cm^2/s (*p*-xylene) by desorption methods;[2] $D = 1.8 \times 10^{-8}$ cm^2/s for *N,N*-dimethylaniline by a fluorescence quenching method.[8] On that basis, the present fluorescence method is a true measure of diffusion within the films.

To determine whether transport of anisole molecules across the film–liquid interface may influence the *D* values, the pH and ionic strength of the aqueous ethanol were increased by adding 1 M KOH to the 0.5 M KI solution. As indicated in Table I, the *D* value obtained from this experiment is the same (within experimental error) as that found in the absence of the KOH. Thus, transport across the interfacial region is not the rate-determining step in this diffusional process.

In principle, the aforementioned dilution of anisole throughout the liquid component and the removal of much of it from the excitation light beam should allow the iodide quencher to be deleted from the aqueous ethanol. However, when such an experiment was conducted, the decay curve (Figure 1b) was not smooth. Apparently, concentration gradients are present in the liquid near the interface with the film until they are dispersed (by Brownian motion, minor vibrations of the cuvette, etc.); the measured fluorescence intensity is greater than expected.

In previous reports, we have demonstrated that diffusion is attenuated significantly by cold-stretching the LDPE films in which small molecules reside.[7-9] Consistent with those observations, the *D* value of anisole in LDPE cold-stretched 5× is 3.3×10^{-9} cm^2/s or ca. $^1/_6$ of its unstretched value. Comparable decreases have been measured by us for *N,N*-dimethylaniline in unstretched ($D = 1.8 \times 10^{-8}$ cm^2/s) and stretched ($D = 2.6 \times 10^{-9}$ cm^2/s) LDPE containing covalently attached 9-anthryl groups.[8] Slightly different *D* values for dimethylaniline, but with comparable decreases, were found in LDPE films containing covalently attached 1-pyrenyl groups.[7] Since the latter experiments are based upon the fluorescence changes which occur only at dimethylaniline-accessible sites with anthryl or pyrenyl groups in a film, we were uncertain whether those measurements are reflective of diffusion in the bulk. On the basis of our observations here, we can now state that they are.

We emphasize that the simple method described in this paper should be applicable to diffusion measurements of many small molecules in a wide variety of polymers. The criteria are few:

(1) The small molecules must fluoresce and absorb light at wavelengths where the polymers do not.

(2) The polymers must not act as quenchers of the excited singlet states of the small molecules.

(3) The small molecules must be somewhat soluble in a solvent which both does not absorb the excitation or emission light and exhibits a very low permeability in the host polymer.

In future studies, we intend to test the generality of the method.

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(10) Potentially fluorescent stabilizers and other additives were removed from the LDPE films by placing them overnight in a chloroform bath. After being air-dried for several minutes, the films were equilibrated with anisole by submerging them in a large volume of an ethanolic solution, $[\text{anisole}]_{\text{EtOH}}$. The films were washed rapidly (to remove any surface-occluded anisole) and placed either in the quencher solution (to measure diffusion coefficients) or in a known volume of cyclohexane (to determine the anisole concentrations in the films, $[\text{anisole}]^0_{\text{LDPE}}$.
(11) The efficiency of iodide as a quencher of anisole fluorescence was demonstrated in a control experiment. The fluorescence intensity of 10^{-3} M anisole in N_2-saturated 3/2 (v/v) ethanol/water was reduced by >90% upon the addition of 0.5 M KI.
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