

Water-Uptake Kinetics in Poly(methyl methacrylate) Films with a Fluorescent Rotor Probe

J. P. Goodelle,¹ R. A. Pearson,¹ M. M. Santore²

¹Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

²Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

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ABSTRACT: A fluorescence method was adapted to measure moisture-uptake kinetics in films of poly(methyl methacrylate), and data were interpreted in the context of a Fickian diffusion model. The films, 2–60 μm thick, were supported on acid-etched microscope slides. They were compared with several freestanding slabs about 1 mm thick. The moisture diffusion in the slabs was Fickian with a diffusivity of $3.2 \times 10^{-9} \text{ cm}^2/\text{s}$. The apparent Fickian diffusivity in the films decreased substantially with decreasing film thickness; however, a careful examination revealed that the initial moisture uptake was governed by a thickness-independent diffusivity for a wide range of film thicknesses.

This suggested that the appearance of non-Fickian behavior originated within about a micrometer of the buried interface, possibly as a result of water accumulation beneath the film or slight thickness variations. Moisture uptake in the thickest films was more rapid than in the slabs, most likely because of residual thermal stresses. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2463–2471, 2002

Key words: moisture diffusion; moisture sensor; residual stresses; rotor probes; supported poly(methyl methacrylate) (PMMA) films

INTRODUCTION

Solvent and moisture uptake by polymers is important in biomedical engineering and dentistry, for which polymers are used as adhesives and implanted components. Moisture uptake may cause expansion, compromising function and biocompatibility. In engineering adhesives, moisture or solvents can compromise joint strength. In microelectronic packages, adhesives, and underfills, moisture can facilitate corrosion or cause device failure via swelling stresses.

When plastic components involve thin films or confined geometries, the properties in the device may differ from bulk testing specimens. One explanation is that, as a result of chemistry and curing conditions, a skin (a region of chemically different composition) may develop near the free surface.¹ In other situations, polymers may be processed in contact with a solid surface possessing a different thermal expansion coefficient. After the polymers cool, stresses develop that could influence adhesion or solvent permeation.^{2,3} Finally, there remains the ongoing dispute in the poly-

mer physics community about the influence of confined geometries on film properties such as the mobility⁴ and glass-transition temperature (T_g),^{5–7} which may ultimately influence moisture uptake.

These complications emphasize the importance of studying real devices or employing test specimens whose properties approximate real applications. In the context of moisture uptake, this means taking care to ensure that sample chemistries match those in the real applications and that physical constraints, such as the attachment of a polymer film to a surface, are also taken into account. These restrictions limit the applicability of common methods such as mass evolution and motivate the development of testing methods that can, in principle, be broadly applied.

Spectroscopic methods for moisture and solvents have the advantage that the signal can be generated exclusively within the relevant portion of a device, such as a polymer film on a massive substrate. A number of spectroscopic techniques, such as IR^{8,9} and NMR,¹⁰ show promise for probing buried interfaces and other inaccessible regions. Fluorescence spectroscopy also holds promise because of its high sensitivity. Probes based on fluorescence have the advantage that the instrumentation is relatively economical and portable.

This article is concerned with the use of fluorescent rotor probes as sensors of moisture and, potentially, other solvents in thin polymer films. Rotor probes are a family of fluorescent molecules, such as dialkylaminoalonnitriles, that have two major pathways to re-

Correspondence to: M. M. Santore (santore@mail.pse.umass.edu).

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turn to the ground state from an excited singlet state:^{11–13} an internal conversion involving bond rotations and, when such rotations are hindered, fluorescence. Royal and Torkelson demonstrated that julolidenemalonitrile, when doped at low levels into poly(vinyl acetate), quantitatively captured physical aging phenomena,^{14–16} and they more recently demonstrated the sensitivity of rotor probes to β -relaxations in poly(ethyl methacrylate) and poly(isobutyl methacrylate).¹⁷ In these studies, it was noted that maintaining dry samples was of the utmost importance because moisture uptake would affect the free volume and fluorescence; this motivated our initial work on moisture uptake.^{18,19} More recently, Miller et al.²⁰ studied the moisture sensitivity of a number of rotor probes in poly(vinyl acetate) and a polyamide-cured epoxy, reaffirming their sensitivity to moisture. Fluorescence was substantial when the polymer matrix was below T_g , but plasticization occurring with solvent uptake enabled rotor motions and caused a loss of fluorescence.

This work demonstrates the use of the rotor probe dicyanovinyl julolidine (DCVJ) for measuring moisture in poly(methyl methacrylate) (PMMA). PMMA was chosen as a model because of its relevance as a photoresist and because it is one of the most frequently studied glassy polymers.^{21,22} This work first demonstrates the moisture sensitivity of the fluorescence and then highlights the robust nature of the fluorescence probe: its utility in samples that are cycled multiple times and the relationship between the fluorescence change and mass of water imbibed by the samples. Finally, the probe is used in a kinetic study of moisture diffusion in supported PMMA films. The moisture diffusion in supported films of various thicknesses is compared with that in freestanding PMMA slabs, and deviations from Fickian diffusion are explored.

EXPERIMENTAL

PMMA with a reported molecular weight of 130,000 and a polydispersity of 1.4 was purchased from Scientific Polymer Products, Inc. Any residual solvents or monomer were removed by 24 h of drying at 110°C. A T_g value of 115°C was found with a TA Instruments differential scanning calorimeter in the dynamic scan mode at 10°C/min.

For the formation of supported films, PMMA was dissolved in toluene at concentrations of 5, 10, and 12 wt %. These concentrations possessed appropriate viscosities to yield, via spin casting, film thicknesses in the range of interest. Mild heating between 40 and 50°C was useful to facilitate the more concentrated 12 wt % solution. After the dissolution of PMMA with continuous stirring for 24 h, DCVJ, purchased from Molecular Probes and used as received, was added to

yield solutions with DCVJ concentrations of 0.002 wt % relative to PMMA. Solutions were stirred at least an additional 24 h to ensure complete DCVJ dissolution before spin casting.

Soda lime glass microscope slides from Fisher with dimensions of 7.5 cm \times 2.5 cm were used for fluorescence experiments, whereas 12 mm \times 12 mm coverslips were employed for most mass-uptake studies. Flats were first wiped with 2-propanol and then soaked in a 2M HCl acid bath for 12 h; this was followed by a rinse with deionized water. This cleaning method was adopted from the work of Roberts,²³ who found that cleaning soda lime slides in this way increased the rolling adhesion between rubber cylinders on a sloped glass track, presumably because of the enhancement of the acidic surface silanol density. Although PMMA films have been reported to adhere strongly to acidic glass,²⁴ we found that by itself, the aforementioned procedure was insufficient to yield adequate bonding of PMMA to microscope slides. Films spin-cast on these acid-treated surfaces debonded after exposure to water; this suggested an accumulation of water at the polymer–glass interface.

The integrity of the polymer–glass interface was increased with an adhesion promoter chemisorbed onto the flats after the aforementioned acid-etch procedure. A 1.3×10^{-2} M solution of Γ -methacryloxypropyl trimethoxysilane (Γ -MPS) in a methanol/water (95/5 vol %) mixture was reacted at room temperature overnight and then spin-cast onto the acid-etched microscope slides. These were then heated at 110°C for 10 min, cooled, and rinsed with methanol before the spin casting of PMMA films. Polymer films were annealed at least 72 h in a vacuum oven at 135°C, cooled slowly to room temperature, and stored in a desiccator with P_2O_5 until use. This procedure yielded films with T_g 's identical to that of the bulk polymer; this suggested that there was no residual solvent and that the DCVJ dye did not alter the polymer matrix. After moisture-uptake studies, film thicknesses were determined with a Mitutoyo or Tencor thickness gauge on edges made by sections of the film being cut away. Several measurements were made on a grid across the face of each film.

Diffusion in supported films was compared with that in thin slabs, which were molded in a press at 300°C and cooled at 1°C/min, the same rate used for the polymer films. The slabs were cut to size and stored in a desiccator with P_2O_5 .

Fluorescence was measured in a Spex Fluorolog II photon counting spectrofluorometer fitted with a film-surface fluorescence cell, which is described in our previous studies of polymer adsorption.^{25,26} The cell can operate in total internal reflection; however, in this work, the refractive index of the PMMA film was less than that of the glass flat, giving transmission of the excitation light through the film. The free surface of

the film was in contact with a 0.5-mm-deep flow channel through which liquid water or humid air flowed. Moisture-saturated air was obtained by passage through several sparging chambers. The design of the channel facilitated calculations of the boundary layer thickness near the film as a function of the flow rate and fluid properties,^{27,28} features that we confirmed experimentally.²⁹

Fluorescence evolution was sometimes compared with mass-based measurements of moisture uptake conducted in a Cahn balance. In the mass-uptake studies, polymer films on coverslips or pieces of microscope slides were suspended in the top one-third of a cylindrical glass chamber (4 cm in diameter) through which vapor flowed. Films were preconditioned in flowing nitrogen, and the vapor phase was switched to humid air at the start of an uptake study. Because of the dead volume of the test chamber, a considerable lag time was needed for the moisture to fill the flow cell, and during this time, uptake was also occurring the polymer film but at rates corresponding to relatively low local vapor concentrations. We developed a procedure to fill the cell with moist air at time zero as rapidly as possible, and we discuss the issue of vapor-side transport limitations in the next section.

RESULTS AND DISCUSSION

Static considerations

Fluorescence emission spectra in Figure 1 (with excitation at 450 nm) reveal the influence of moisture for a 32- μm PMMA film containing 0.002 wt % DCVJ. For the dry film, the spectra exhibit a maximum at 479 nm, and as moisture permeates the film, this maximum shifts to 485 nm. This redshifting results from polar interactions between DCVJ and water and is consistent with the previous observations of Miller et al.²⁰ for water uptake in poly(vinyl acetate) or epoxy polyamide. Figure 1 also illustrates that as moisture permeates PMMA, the fluorescence intensity increases substantially. (At 485 nm, where most of the work in this article was done, an average ultimate fluorescence increase of 27% was found for a mass uptake of 2.1%. In Figure 1, the fluorescence increase at 485 nm is 26%). This result contradicts expectations that penetrants will increase the dye's local mobility and reduce fluorescence.²⁰ Figure 1, therefore, suggests that in PMMA, moisture acts like an antiplasticizer, or that the fluorescence intensity is increased through other means. Our observed fluorescence reduction with methanol or butanol uptake in DCVJ-doped PMMA^{18,30} suggests a lack of specific interactions between DCVJ and PMMA.

Indeed, Shen et al.³¹ observed that at moisture concentrations below 1%, PMMA was plasticized, but above a 1% water uptake, the modulus was increased.

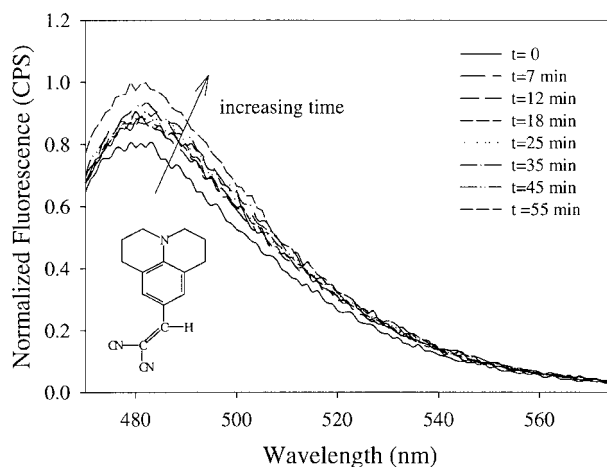


Figure 1 Evolution of the fluorescent spectrum ($\lambda_{\text{ex}} = 450$ nm) during liquid water uptake in a 32- μm PMMA film doped with 0.002 wt % DCVJ. The inset shows a DCVJ molecule.

Antiplasticization of PMMA by moisture is also consistent with Turner's³² observations that only half of the moisture imbibed by PMMA samples contributed to an increase in sample volume, with additive partial molar volumes of the water and PMMA. The other half of the imbibed moisture raised the PMMA density, presumably by accumulating in small microvoids per a dual-sorption-uptake mechanism.³² It is difficult to anticipate the impact of moisture in microvoids on the DCVJ fluorescence. If Turner's scenario is correct, the DCVJ probe will detect only one of several populations of water molecules.

Besides Turner's hypothesis of accumulation in microvoids, an alternate explanation is that dissolved water contributes a negative partial molar volume and that the close packing of water molecules and the PMMA matrix may decrease local mobility. A negative partial molar volume of mixing (or microvoids so small that single water molecules are solvated in each and reduce the free volume and chain mobility) would explain the increase in fluorescence on moisture uptake.

Another possible cause for the fluorescence increase in Figure 1 is the relative solubility of DCVJ in PMMA in contrast to water. DCVJ is highly water-insoluble but soluble in PMMA.³⁰ It may be that the uptake of moisture into a DCVJ-containing PMMA specimen causes closer association between DCVJ and PMMA because of the hydrophobic repulsion of DCVJ from water molecules. Therefore, in the presence of water, DCVJ more closely associated with PMMA may be less mobile. This solubility explanation is consistent with the observed DCVJ fluorescence decrease with butanol or methanol sorption in PMMA.^{18,30} DCVJ dissolves in both solvents.

Whatever the physics are behind the DCVJ moisture-induced fluorescence increase, certain issues

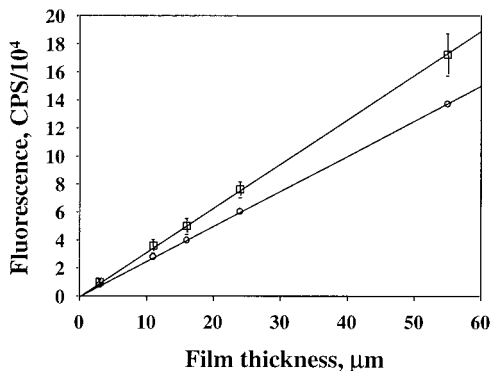


Figure 2 Fluorescent signal versus film thickness in PMMA films (○) dry as processed and (□) after equilibrating with liquid water.

must be resolved to develop DCVJ fluorescence as a tool for measuring moisture uptake. First, it must be established that fluorescence at a single wavelength near the maximum is sufficient. Next to be established is that DCVJ is uniformly dispersed throughout PMMA. The issue of the reversibility of the fluorescence change and retention of fluorophores in the polymer matrix must also be addressed. Finally, the fluorescence must be calibrated in terms of the mass uptake.

We compared the evolution of the peak area from 470 to 575 nm with that at the maximum and with the fluorescence intensity at 485 nm. The data,³⁰ not shown here, indicated that all three were equivalent measures of moisture. For kinetic studies, however, a fixed wavelength is most convenient. Figure 2 illustrates the fluorescence, with excitation at 450 nm and emission at 485 nm, as a function of film thickness for dry and moisture-saturated films. The fluorescence for both is proportional to thickness and increases by about 27% (independently of thickness) on water uptake. All films took up approximately 2.1 mass %. Although this does not prove uniform dye distribution throughout the films, it does suggest that our fabrication procedures are sufficiently consistent to allow a comparison between films of different thicknesses. Also, a y -intercept of zero suggests no surface excess of dye at the glass–film interface or the free film surface.

Figure 3 demonstrates that the spectrum of a 7- μ m film after exposure to liquid water is identical to that obtained after subsequent annealing at 135°C for 24 h *in vacuo* for the removal of water. This result proves the retention of DCVJ during exposure to water and in the drying process.

To establish the proportionality between the fluorescence change and mass uptake, one would ideally design an experiment in which the moisture concentration was varied from datum to datum but was uniform across the film for each datum. Such a sce-

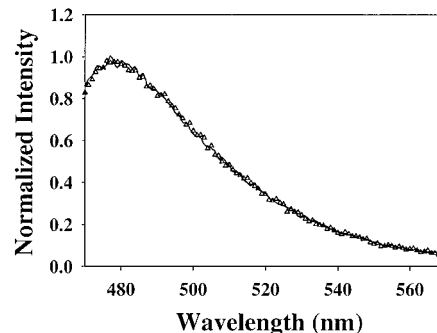


Figure 3 Fluorescence spectra for a 7- μ m PMMA film with excitation at 450 nm: (—) signal from the initially dry film and (Δ) signal after saturation with water and subsequent drying above T_g .

nario might correspond to films equilibrated in air of different relative humidities. We were unable, however, to systematically achieve controlled relative humidity and measure the equilibrium moisture mass. Therefore, we adopted Miller et al.'s approach²⁰ to compare the mass uptake and fluorescence at intermediate times during uptake. We studied the moisture uptake for calibration films first via fluorescence and later on a microbalance. After the conditioning of each film with dry nitrogen *in situ*, the film's free surface was exposed to saturated air, and the fluorescence was measured at several specific times during uptake. The film was then removed from the spectrometer, and a 12 mm \times 12 mm section was cut and placed in a Cahn microbalance. After the film was reconditioned in dry nitrogen, moisture uptake was repeated, with the mass recorded at the same time increments. The film was subsequently dried in nitrogen for confirmation of the reversibility of mass uptake. This procedure assumes that the moisture-uptake kinetics during sequential runs are identical, as shown to be the case in the Kinetics section.

Figure 4 compares the mass and fluorescence changes within a single film and demonstrates the linearity of the fluorescence change with moisture uptake. The greatest data scatter occurs near mass up-

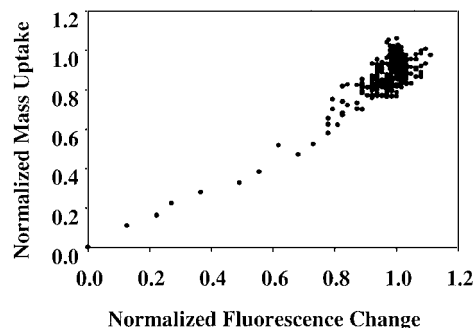


Figure 4 Comparison of mass uptake and fluorescence change in an 8- μ m film.

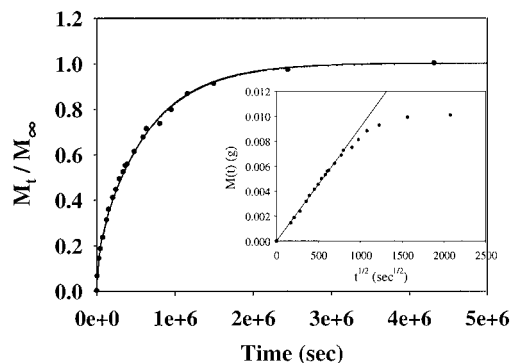


Figure 5 Water uptake in a free-standing, 0.143-cm-thick PMMA slab as a function of time and the best fit to the Fickian model in eq. (1), with $D = 3.2 \times 10^{-9}$ cm²/s. The inset shows $t^{1/2}$ power-law scaling per eq. (2).

takes of 2% and fluorescence changes near 27%. This is because, near the ends of runs, the fluorescence and mass evolutions are most difficult to reproduce. Figure 4 indicates no saturation of the fluorescence signal as the film approaches the maximum moisture uptake near 2%.

Kinetics

Freestanding slabs

We first considered uptake kinetics in freestanding PMMA slabs as a measure of diffusion through bulk PMMA. Figure 5 shows the normalized mass uptake in a 0.143-cm-thick slab, which was submerged in liquid water so that diffusion proceeded toward the center of the slab from both faces. For the run in Figure 5 and others like it, the equilibrium mass uptake (M_∞) was 2.2%. Figure 5 makes a comparison with the solution of the one-dimensional Fickian diffusion equation for normalized mass evolution, $M(t)/M_\infty$, as a function of time t :³³

$$\frac{M(t)}{M(\infty)} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right) = \frac{F(t) - F(0)}{F(\infty) - F(0)} = \Phi(t) \quad (1)$$

where D is a constant diffusion coefficient and $2L$ is the slab thickness. $F(t)$ is the evolving fluorescence signal, which in normalized form is denoted $\Phi(t)$. Equation (1) presumes a dry slab at time zero, and on exposure to moisture, the faces of the slab equilibrate immediately so that the concentration of water is constant at the polymer surface. Equation (1) can also be used to interpret the kinetics of moisture uptake in supported films of thickness L , where diffusion starts at the film's free surface and the buried interface is

impenetrable to moisture. Because calibrations established the proportionality between fractional fluorescence change and mass uptake, the kinetic form in eq. (1) also applies to the evolving fluorescence signal in studies of supported films.

The kinetics in Figure 5 agree well with eq. (1) and the assumption of a concentration-independent diffusivity, in this case $D = 3.2 \times 10^{-9}$ cm²/s, which represents, within a variability of 5%, the average for five samples. Our diffusivity value was consistent with the literature,^{32,34–38} although a number of diffusion coefficients have been previously reported, from 3 to 9×10^{-9} cm²/s.

Variations in previously reported diffusivities may be attributed to the PMMA origin and handling, including the molecular weight distribution, and the monomer or solvent present in other studies.³⁴

Moisture uptake in PMMA is thought to follow Fick's law.^{32,34–38} Fickian behavior is often determined by testing of the conformity of the initial kinetics to $t^{1/2}$ scaling. At short times, when most of the water is concentrated near the free surface of the film, the moisture profile follows an error function, and the mass uptake (or fluorescence change) follows:³³

$$M(t) = 4C_\infty A \left(\frac{Dt}{\pi}\right)^{1/2} \quad (2)$$

where C_∞ is the equilibrium mass concentration of water in the polymer and A is the area of the sample face. The $t^{1/2}$ dependence breaks down for slabs when the moisture concentration at the center of the film becomes substantially nonzero. The inset of Figure 5 tests the $t^{1/2}$ power law for moisture uptake in the bulk slabs, and our kinetic data confirm the Fickian mechanism. The constant diffusivity adequately describes the data, probably because the maximum concentration, near 2 wt % water, is insufficient to plasticize the films or dramatically alter PMMA.

Supported films

Figure 6 illustrates the fluorescence evolution (with emissions measured at 485 nm) for two sequential moisture sorption runs with humid air in contact with a 16- μ m film. Between the first and second runs, the film was dried in situ at room temperature with flowing dry nitrogen until the fluorescence signal approached the original spectrum for the dry film. Also shown in Figure 6 is the best fit to eq. (1), yielding $D = 5.7 \times 10^{-9}$ cm²/s. The first and second uptake runs exhibited nearly identical kinetics, with small differences defining the error of the experiment and justifying our approach of repeated runs on the same film with reconditioning in drying nitrogen. Notably, in Figure 6, the quality of the fit to eq. (1) is not quite as

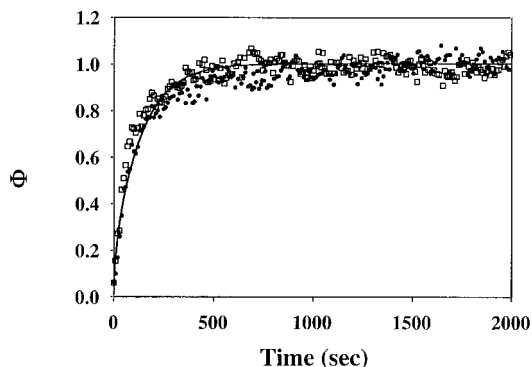


Figure 6 Normalized fluorescence change at $\lambda_{em} = 485$ nm for moisture uptake as a function of time: (\square) first and (\bullet) second water-vapor-uptake runs on a $16\text{-}\mu\text{m}$ film with intermediate reconditioning in dry nitrogen. The line is the best fit to eq. (1) with a diffusivity of 5.7×10^{-9} cm^2/s .

good as it was for the bulk PMMA sample. In particular, if one attempts to fit the early stages of uptake with the Fickian model, the late-stage kinetics show noticeable deviation from the Fickian kinetics.

To further test if Fickian kinetics adequately describe moisture uptake in supported PMMA films, we examined the influence of the film thickness in Figure 7. Figure 7(A,B) shows the mass evolution and fluorescence change during exposure to humid air, whereas Figure 7(C) shows the fluorescence evolution on exposure to liquid water. For most of the data in Figure 7(A–C), the same films were reused. In Figure 7, the overall fluorescence change or fractional mass uptake is normalized to unity on the y -axis, whereas the x -axis is scaled on the film thickness squared per eq. (1). Adherence to Fickian kinetics would collapse the data to a single uptake curve.

The most striking feature in Figure 7 is that the data do not collapse into a single curve, especially in Figure 7(A,B), which shows fluorescence and mass-based measurements of uptake from humid air. When humid air was used instead of liquid water, the x -axis scaling on the square of film thickness caused the initial kinetics for the thinnest films to appear dramatically slower than the uptake kinetics for the thicker films.

That the anomaly for thin films occurs with humid air rather than liquid water provides a clue to the origin of the kinetics: With uptake from moist air, the kinetics are influenced by diffusion of the moisture through the vapor near a film's surface. At the beginning of an uptake experiment, the flow chamber contains the film in contact with dry nitrogen. After a valve turnover, moist air begins to flow over the sample, and time is needed before the moisture reaches the film surface. For the fluorescence-based measurements employing a slit shear cell, the time needed to establish this boundary layer is well defined.^{27,28} For our cell geometry, and a moisture diffusivity in air of

$0.256 \text{ cm}^2/\text{s}$,³⁹ we estimate that approximately 1 s is needed to establish the boundary layer. For a PMMA film with a thickness of $2\text{--}3 \mu\text{m}$, the time needed to saturate 95% of the film (with a bulk diffusivity of $3 \times 10^{-9} \text{ cm}^2/\text{s}$) will be approximately 10 s. The similarity of these two timescales means that the vapor-side diffusion will influence the kinetics in the thinner films. For mass uptake in the Cahn microbalance, the flow geometry is larger in scale, and the maximum flow rate is limited. As a result, the vapor-side mass transport in the Cahn balance is slower than that in the fluorescence chamber; this explains why the thinnest

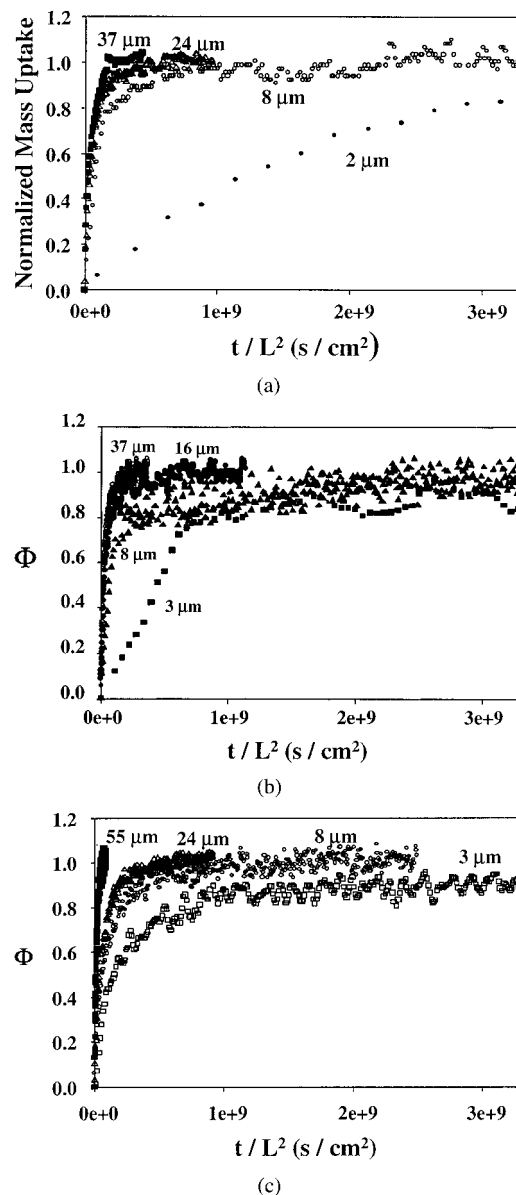


Figure 7 Moisture-uptake kinetics in thin supported PMMA films of various thicknesses: (A) normalized mass evolution for uptake from humid air, (B) normalized fluorescence evolution for uptake from humid air, and (C) normalized fluorescence evolution for uptake from liquid water.

2- μm film in Figure 7(A) (Cahn balance) deviates more than the 3- μm film in Figure 7(B) (fluorescence cell).

Because the first minute of each moisture-uptake run reflects moisture movement through the vapor rather than the kinetics of diffusion through the polymer, uptake from liquid water provides a clearer picture of the early-stage diffusion kinetics. Figure 7(A–C) agrees, however, that the deviation from the scaling in eq. (1) goes beyond the vapor-side influence at short times; this is most evident with the thin films. Even in Figure 7(C), there is a trend, becoming increasingly pronounced with decreasing film thickness, that the shoulders of the kinetic traces become laggy and deviate from eq. (1). Therefore, if one fits eq. (1) directly to the data in Figure 7(C), paying attention to fit the shoulder in addition to the initial kinetics, there is a decrease in the apparent diffusion coefficient with decreasing film thickness, as summarized in Figure 8.

In Figure 8, the dependence of the apparent Fickian diffusivity on film thickness is dramatic: the diffusivity varies over 2 orders of magnitude as the film thickness is changed from about 2 to 60 μm . Furthermore, the diffusivities in the thickest films are faster than those measured in the bulk slab. For all but the thinnest films, for which vapor-side limitations were a concern, the mass and fluorescence data were consistent. Moreover, our diffusivity values agree well with those reported by Tong and Saenger,³⁵ who, using a beam-bending method, found slower moisture diffusivities in thinner supported PMMA films, albeit for a narrower range of film thicknesses.

To gain perspective concerning the possible reasons for the behavior in Figure 8, we attempted to distinguish the behavior originating at the film's free surface from that deeper into the film. To this end, the data from Figure 7 were reevaluated, as a function of $t^{1/2}$ in Figure 9(A–C), per eq. (2). In this representation, at short times all the data should collapse into a single

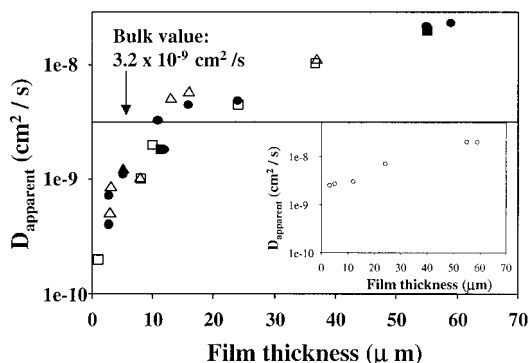


Figure 8 Summary of apparent Fickian diffusivities from the best fit to the entire data set for each run: (Δ) moist air and fluorescence, (\bullet) liquid water and fluorescence; (\square) moist air and Cahn balance, and (\blacksquare) ref. 34 and beam bending. The inset shows diffusivities determined by initial slopes of $t^{1/2}$ plots in Figure 9.

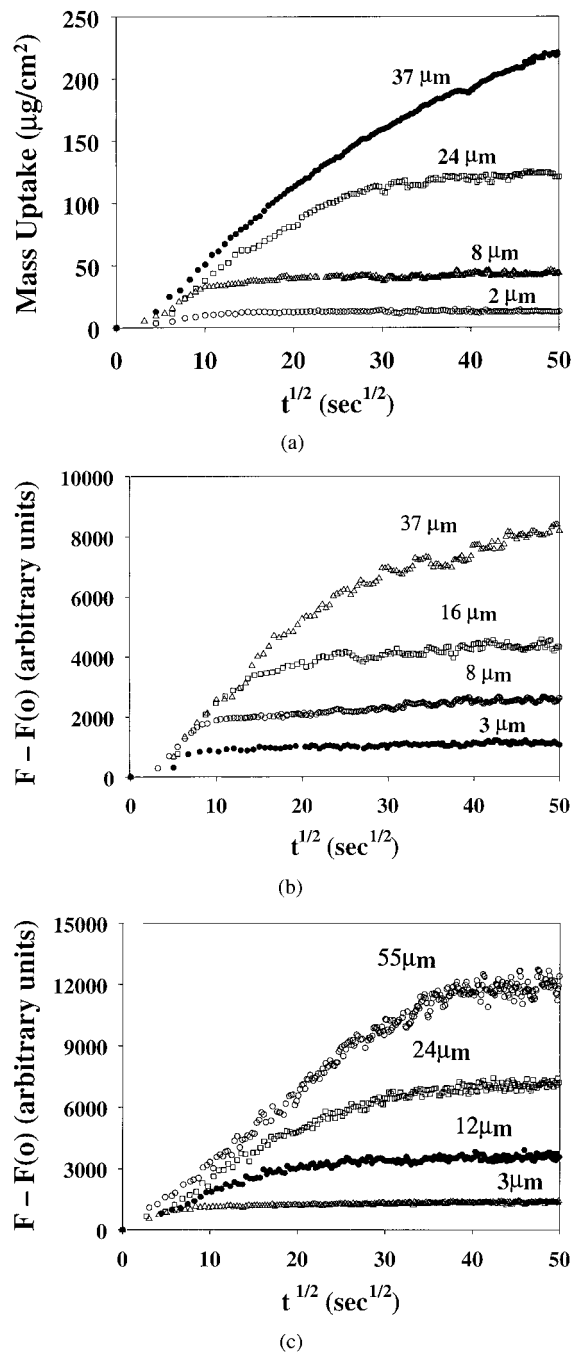


Figure 9 Moisture-uptake kinetics in thin supported PMMA films of various thicknesses: (A) absolute mass evolution for uptake from humid air, (B) absolute fluorescence evolution for uptake from humid air, and (C) absolute fluorescence evolution for uptake from liquid water.

curve, regardless of film thickness, because at short and intermediate times, the moisture front has not yet reached the polymer–glass interface. When the moisture front reaches the buried interface, the uptake will slow and the curves will turn over; this should occur earlier for thinner films. Figure 9 confirms that this is indeed the case, indicating that moisture diffusion into the films is initially Fickian at the outermost portion of

the films. This argues against any crazing near the film's surface that increases the external surface area and initial rate of uptake in thicker films.

In Figure 9, the curves for uptake from moist air are more rounded than the expected linear form, which occurs for uptake from liquid water. The rounded shape is most likely an artifact of the mass-transport limitation at the film's free surface, already shown to occur in Figure 7, because the representation in Figure 9 exaggerates the short-time features. Therefore, the diffusion coefficients obtained from the initial slopes of the runs in Figure 9(C), for uptake from liquid water, are summarized in the inset of Figure 8 and emphasize the interpretation that the initial uptake kinetics yield a film-thickness-independent diffusivity.

Returning to the uptake from liquid water, we attempted to address the issue of whether the breakdown of eq. (2) as the moisture front reached the buried interface was consistent with the independently measured film thicknesses. In a theoretical plot of the expected Fickian uptake from eq. (1) versus $t^{1/2}$, the initial portion of the curve is linear, and deviations from linearity occur near mass fractions of about two-thirds (and $t^{1/2}$ values also near two-thirds). This was found to be the case for the experimentally measured uptake in the bulk slab in the inset of Figure 5. In Figure 9(C), the linearity of the curves also persists for at least two-thirds of the overall mass uptake for the 55- and 24- μm films. For the thinner films, however, the deviation from Fickian kinetics occurs prematurely, for instance, near a 50% uptake for the 12- μm film in Figure 9(C). This suggests that the reason the apparent Fickian diffusivities are slow for thin films is that processes near the buried interface are not properly accounted for in eqs. (1) and (2). More quantitatively, from Figures 7(C) and 9(C), we suspect deviations from the Fickian equation about 1–2 μm near the buried interface in all our samples. This region of the film is a small fraction of the thick 20–50- μm films (and difficult to see in the kinetic traces) but contributes significantly to the overall uptake kinetics in the thinner films. Therefore, the diffusivities measured from the initial uptake kinetics in Figure 9 and summarized in the inset of Figure 8 represent diffusion through a substantial portion of the film. The non-Fickian behavior, which leads to an apparent thickness dependence of the diffusivity, actually results from kinetics near the buried interface, which is a small fraction of the total film mass. Diffusion through most of the film is thickness-independent.

There have been reports of polymer properties near buried interfaces that differ from those of the bulk film,⁴⁰ even interfacial mobilities that are slower than those of the bulk.⁴ We would, however, expect such an effect, were it to occur in our systems, to operate on length scales of less than 100 nm and perhaps to contribute only a slight influence to the thinnest films

(2 μm) studied here. We have no reason to believe that such confinement effects^{6,7} propagate 1–2 μm from a buried interface. Two other possible reasons for the slow long-time moisture uptake are (1) water accumulation beneath the film and (2) variations in film thickness. Were moisture to accumulate beneath the films, as our preliminary neutron reflectivity studies indicate (in a 2-nm-thick zone at the buried interface beneath a PMMA film and an oxidized silicon wafer with Γ -MPS, moisture accumulates to levels as high as 45 vol %, whereas the adhesion of PMMA to the wafer appears strong to the touch),⁴¹ the boundary condition at the buried interface would be different from the no-penetration condition leading to eq. (1). We currently are not able to measure the uptake kinetics of interfacial moisture with neutron reflectivity and believe that the amount of interfacial moisture is reduced by Γ -MPS, which successfully promotes PMMA adhesion to glass. However, pockets of interfacial moisture would be invisible to a probe doped in the matrix film but would slow the final stages of film equilibration. There would be no effect of hungry interfaces in the early stages of uptake before the moisture front reaches the interface.

The second possibility for the slow final equilibration of the PMMA films with water may simply be that the outer surface of the film is not perfectly smooth, with 0.5- μm variations in thickness over an area of several square millimeters. Were this the case, the initial moisture uptake would proceed as expected, but as equilibration occurred, the thinner regions of the film would saturate before the thicker regions, convoluting the final uptake kinetics and making them appear more gradual. It is likely that both slight thickness variations and some moisture accumulation beneath the film contributed to the gradual long-time behavior. Because Figure 9(C) demonstrates the consistency of the early uptake data for all films, we believe that the moisture uptake in the films is fundamentally Fickian.

Of final note, in Figure 8 there remains a small but reproducible effect of thickness on diffusivity for the thicker films, with the diffusivities in thick supported PMMA films faster than those in the slabs in Figure 5. The most likely reason is residual stress initiating at the buried interface and propagating through the film. Several groups have reported increases in solvent diffusivities in stressed samples.^{42,43} With the method of Ree et al.³ for estimating the residual stresses in our thicker films, values of 17 MPa were found for approximately 50–60- μm films. (This calculation employed a temperature-dependent coefficient of thermal expansion derived from the PMMA data of Olabsisi and Simha,⁴⁴ a coefficient of thermal expansion for glass of 9 ppm, a temperature-dependent Young's modulus for PMMA,⁴⁵ and a Poisson's ratio of 0.35 for PMMA.) Residual tensile stresses result in volumetric expansions

similar to those caused by temperature increases.⁴⁶ Therefore, it seems reasonable that larger diffusivities would be found in the thicker films, which possess residual stresses. Residual stresses may also cause crazing at the film's free surface; however, the superposition of the early-stage uptake kinetics in Figure 9 argues against such surface crazing. Notably, the 17-mPa residual stress estimate is less than 27 mPa, the threshold value calculated by Shen et al.³¹ for craze nucleation in fully moisture-saturated PMMA.

CONCLUSIONS

We adapted the DCVJ rotor probe for use as a sensor of moisture in thin PMMA films. Although the DCVJ fluorescence increased on moisture uptake, contrary to expectations for plasticized systems, the fluorescence change and mass change were found to be directly proportional over the full range of mass uptake. Furthermore, where mass measurements were possible, fluorescence and mass evolution were consistent. This suggests that the addition of DCVJ to a film is noninvasive for the purposes of moisture-uptake studies and that the distribution of DCVJ throughout a film is sufficiently uniform. Moreover, because most balances operate in air and are subject to vapor-side transport effects, the fluorescence method is preferred for measuring kinetics in samples for which the experimental time is short. Through the use of a liquid water phase and the fluorescent probe, the transport issues outside the film are eliminated.

For a series of supported films, the moisture-uptake kinetics appeared non-Fickian when the entire data sets were fit to the appropriate kinetic form. A closer scrutinization of the short-time data for uptake from liquid water revealed identical kinetics for all films up to the time when the moisture front came within about a micrometer of the buried interface. The final phases of the uptake kinetics were, however, slower than the initial kinetics, leading to smaller apparent Fickian diffusivity for the thinner films. The more gradual approach to the final film saturation might have resulted from moisture accumulation beneath the film or long-range (over several millimeters in the planar direction) variations in the film thickness (ca. 0.5 μm). Such experimental complications are a more plausible explanation for our observations than the conclusion of non-Fickian behavior in restricted geometries.

References

- Lefebvre, D. R.; Takahashi, K. M.; Muller, A. J.; Raju, V. R. *J Adhes Sci Technol* 1991, 5, 201.
- Fu, T. Z.; Durning, C. J.; Tong, H. M. *J Appl Polym Sci* 1991, 43, 709.
- Ree, M.; Chu, C. W.; Goldberg, M. J. *J Appl Phys* 1994, 75, 1410.
- Frank, B.; Gast, A. P.; Russell, T. P.; Brown, H. R.; Hawker, C. *Macromolecules* 1996, 29, 6531.
- Hall, D. B.; Hooker, J. C.; Torkelson, J. M. *Macromolecules* 1997, 30, 667.
- Wang, I. Y.; Ploehn, H. J. *J Appl Polym Sci* 1996, 59, 345.
- Moylan, C. R.; Best, M. E.; Ree, M. *J Polym Sci Part B: Polym Phys* 1991, 29, 87.
- Van Alsten, J. G.; Coburn, J. C. *Macromolecules* 1994, 27, 3746.
- Van Alsten, J. G.; Lustig, S. R. *Macromolecules* 1995, 28, 5069.
- Schadt, R. J.; VanderHart, D. L. *Macromolecules* 1995, 28, 3416.
- Loutfy, R. O.; Law, K. Y. *J Phys Chem* 1980, 84, 2803.
- Loutfy, R. O. *J Polym Sci Polym Phys Ed* 1985, 20, 825.
- Loutfy, R. O. *Pure Applied Chem* 1986, 58, 1239.
- Royal, J. S.; Torkelson, J. M. *Macromolecules* 1992, 25, 1705.
- Royal, J. S.; Torkelson, J. M. *Macromolecules* 1993, 26, 5331.
- Royal, J. S.; Victor, J. G.; Torkelson, J. M. *Macromolecules* 1992, 25, 729.
- Hooker, J. C.; Torkelson, J. M. *Macromolecules* 1993, 26, 7683.
- Goodelle, J. P.; Pearson, R. A.; Santore, M. M. *SRC TechCon Proc* 1996.
- Goodelle, J. P.; Santore, M. M. *SRC TechCon Proc* 1998.
- Miller, K. E.; Krueger, R. H.; Torkelson, J. M. *J Polym Sci Part B: Polym Phys* 1995, 33, 2343.
- Andrews, E. H.; Levy, C. M.; Willis, J. *J Mater Sci* 1973, 8, 1000.
- Vrentas, J. S.; Vrentas, C. M. *J Appl Polym Sci* 1992, 45, 1497.
- Roberts, A. D. *Langmuir* 1992, 8, 1479.
- Fowkes, F. M. In *Microscopic Aspects of Adhesion and Lubrication*; Georges, J. M., Ed.; Elsevier: Amsterdam, 1982.
- Fu, Z.; Santore, M. M. *Macromolecules* 1998, 31, 7014.
- Fu, Z.; Santore, M. M. *Macromolecules* 1999, 32, 1939.
- Lok, B. K.; Cheng, Y.-L.; Robertson, C. R. *J Colloid Interface Sci* 1983, 91, 87.
- Lok, B. K.; Cheng, Y.-L.; Robertson, C. R. *J Colloid Interface Sci* 1983, 91, 104.
- Fu, Z.; Santore, M. M. *Colloids Surf A* 1998, 135, 63.
- Goodelle, J. P. Ph.D. Dissertation, Lehigh University, 1999.
- Shen, J.; Chen, C. C.; Sauer, J. A. *Polymer* 1985, 26, 513.
- Turner, D. T. *Polymer* 1982, 23, 197.
- Crank, J. *The Mathematics of Diffusion*; Oxford University Press: London, 1975; Chapter 4.
- Turner, D. T. *Polymer* 1987, 28, 293.
- Tong, H. M.; Saenger, K. L. *J Appl Polym Sci* 1989, 38, 937.
- Braden, M. J. *Prosthet Dent* 1964, 14, 307.
- Bueche, F. *J Polym Sci* 1954, 14, 414.
- Kovacs, A. *J Chim Phys* 1948, 45, 258.
- Bennett, C. O.; Myers, J. E. *Momentum, Heat, and Mass Transfer*, 3rd ed.; McGraw-Hill: New York, 1982; p 811.
- Despotopoulou, M. M.; Miller, R. D.; Rabolt, J. F.; Frank, C. W. *J Polym Sci Part B: Polym Phys* 1996, 34, 2335.
- Wu, W. L. NIST. Unpublished neutron reflectivity data.
- Wolf, C. J.; Fu, H. *J Polym Sci Part B: Polym Phys* 1996, 34, 75.
- Tam, S. Y.; Scriven, L. E.; Stolarski, H. K. *Mater Res Soc Symp Proc* 1995, 356, 547.
- Olabisi, O.; Simha, R. *Macromolecules* 1975, 8, 206.
- Nielsen, L. E. *Mechanical Properties of Polymers*; Reinhold: New York, 1962; p 178.
- Yee, A. F.; Bankert, R. M.; Ngai, K. L.; Rendell, R. W. *J Polym Sci Part B: Polym Phys* 1988, 26, 2463.