

Spectrophotometric Measurement of Swelling of Polymer Films by Very Poor Solvents

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ABSTRACT: Solvent swelling of polymers is important for many applications, but can be difficult to measure when thin films or very poor solvents are involved. A novel spectrophotometric method is presented that is well suited for measuring swelling of thick or thin polymer films by very poor solvents. In this method, the solvent is stained with iodine, and solvent uptake is measured by observing the change in visible light absorption of the polymer using a spectrophotometer. Using this method, swelling can be accurately measured in thin ($< 2 \mu\text{m}$) polymer films and with poor solvents that cause little swelling, even water. Results

are presented for PMMA films of varying molecular weights swelled by water, by water–alcohol mixtures, and by undiluted alcohols. Swelling of these films is more rapid and more Fickian than has been reported for bulk samples, probably due to differences in PMMA molecular weight and processing. The properties of the iodine–PMMA complex are also explored. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1082–1089, 2005

Key words: swelling; films; interfaces; PMMH; alcohol

INTRODUCTION

Solvent swelling of polymer films is important for applications such as lithographic resists, food packaging, membrane separations, and controlled release of drugs. While there are several methods for studying swelling of bulk samples by relatively good solvents, swelling of thin films, or swelling by very poor solvents has been more difficult to measure.

Traditionally, swelling of polymers has been measured by weighing a sample before and after exposure to solvent, by measuring the physical dimensions before and after exposure, or by using a dyed solvent and examining a cross section of the sample microscopically.¹ None of these techniques are well suited for analysis of swelling in thin films, or swelling by very poor solvents, where the changes in mass or dimensions on swelling are very small. Some results from swelling and dissolution of thin films have been reported using ellipsometry^{2,3} and interferometry,⁴ but analysis is not straightforward, as both the thickness and refractive index of the films change during swelling. One study used NMR to measure polymer swelling, but the spatial resolution was only about $100 \mu\text{m}$.⁵

This article describes a modification of the dyed-solvent technique, which allows accurate measure-

ment of solvent swelling using a standard visible spectrophotometer. This technique is suitable for use with thick or thin ($< 2 \mu\text{m}$) films and with very poor solvents, such as water.

EXPERIMENTAL

Polymer films were prepared by spin coating. Poly(methyl methacrylate) (PMMA) powder (145,000 and 996,000 average molecular weight, Aldrich; 75,000 M_w , Polysciences) was dissolved in a mixture of 67% propylene glycol methyl ether acetate and 33% γ -butyrolactone (solution typically about 15% polymer by weight). A few drops of polymer solution were placed on a soda-lime glass slide (prepared as described below), spun at 500 rpm for 30 s, annealed at 95°C for 1 h, allowed to cool slowly overnight, and stored until needed. The films formed in this way typically have a thickness of about $10\text{--}15 \mu\text{m}$ (from mass and area of film), although thicker or thinner films could be made by using more or less dilute polymer solutions.

These films were used in two different ways. “Attached” films were left on the glass substrates, so only one side of the film was exposed to the solvent. “Suspended” films were floated off of the glass with water and glued at the edges to a plastic mount; these films were exposed to solvent on both sides.

For suspended films, the polymer was spin-coated on glass slides that had been treated only by rinsing with acetone. After drying, these films could be floated off of the glass substrate in water and then mounted for use.

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For attached films, the glass had to be specially treated to prevent the films from detaching in solvent. The glass slides were first cleaned by sonication in 1M NaOH, rinsed with dilute HCl, deionized water, and acetone, and then oven dried. The slides were then soaked for 20 min in a 0.014M solution of 3-(trimethoxysilyl)propyl methacrylate in ethanol and rinsed again with acetone. Methyl methacrylate was then polymerized on the surface of the slides, and the slides were rinsed again with acetone and used for spin-coating. Polymer films formed on this treated glass showed greatly enhanced solvent resistance, although films of lower molecular weight or exposed to stronger solvents still had only limited lifetimes.

Solvents used were deionized water, denatured ethanol (Fisher: 90% ethanol, 5% methanol, 5% isopropanol), and 99.9% methanol (Fisher). Solvents were used as received, or as 1 : 1 mixtures of alcohol and water.

Solvent swelling was measured by using solvents containing iodine (0.005M I₂). Previous studies have shown that adding iodine to the solvent had no effect on the position of the solvent front.¹ For pure water, potassium iodide was also added to increase the solubility of I₂. The polymer sample was immersed in the dyed solvent, periodically removed, rinsed briefly with undyed solvent, and placed in a spectrophotometer (Perkin-Elmer Lambda 900) and a spectrum was recorded between 500 and 350 nm. Glass, PMMA, alcohols, and water are transparent over this range, while iodine in solution has a broad absorption near 450 nm, with the exact position depending on the solvent. The intensity of this absorption in the PMMA was used as a measure of total solvent uptake. A spectrum of a fresh PMMA-coated glass slide, or suspended film, was used as a background for thin film experiments; fresh PMMA sheet was used as background for bulk PMMA experiments.

Film thicknesses were determined by recording the mass of the PMMA-coated glass slide before exposure to solvent and again after the PMMA had been removed (after the experiment or after the film had been removed for mounting). The mass of PMMA was obtained by difference, and, from the area of the slide and the density of PMMA, the thickness of the PMMA film could be estimated. All experiments were carried out at room temperature, and containers were sealed during experiments to prevent solvent loss.

RESULTS

Although some film deterioration was observed, especially at longer times, the technique was highly successful in measuring film swelling in water and in water-alcohol mixtures. Film swelling in undiluted alcohols was more difficult to measure, as the films tended to weaken and tear, but with care some measurements were obtained. Some results were also ob-

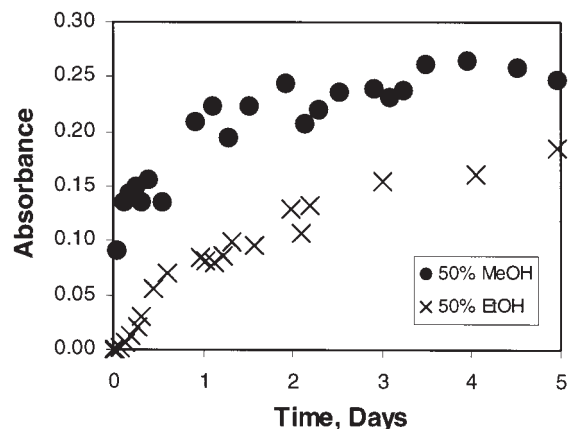


Figure 1 Change in absorbance of PMMA films (1.3 μm thick, 145,000 M_w , attached to glass) soaked in 50% alcohol solution dyed with iodine.

tained with sheet PMMA for comparison to previously published values.

The results obtained were generally consistent, and there were large differences in swelling behavior between films in pure water, water-alcohol mixtures, and undiluted alcohols. The details of how swelling occurred showed significant variations from sample to sample, but the amount of swelling at equilibrium depended only on solvent and film thickness.

Water-alcohol mixtures

PMMA samples placed in iodine-stained solutions of 50% ethanol or methanol in water showed similar "S"-shaped curves for absorption over time (Fig. 1). Initial slow uptake of iodine is followed by a period of rapid uptake, and then finally a gradual leveling off. While all curves observed were generally similar, the sizes and shapes of the three regions varied, and the initial slow uptake region was sometimes absent, especially in methanol solution or with thinner films. Swelling rates showed considerable variation from sample to sample. The time required to reach a constant absorbance showed little or no correlation to film thickness, so the average solvent penetration rate of $10 \pm 17 \mu\text{m}/\text{day}$ is reported only for purposes of comparison. The average penetration rates for 50% ethanol and 50% methanol were the same within experimental error. When other parameters were the same, suspended films swelled more rapidly than attached films (Fig. 2), which is the expected result, since suspended films can swell from both sides at once. However, the average solvent penetration rates for suspended and attached films were not significantly different.

While no significant trends were observed for swelling rates, the final amount of swelling (once absorbance stopped increasing) was more consistent. When

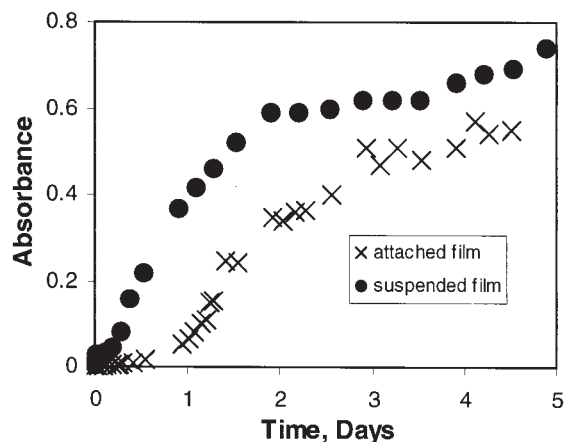


Figure 2 Change in absorbance of PMMA films ($\sim 15 \mu\text{m}$ thick, $145,000 M_w$) soaked in 50% ethanol dyed with iodine. \times , film attached to glass substrate, exposed to solution on just one side. \bullet , suspended film, exposed to solution on both sides.

the final absorbance for each film is plotted against the film thickness, all the points for 50% alcohol solutions fall along the same line (Fig. 3), with an average absorbance of 35 per millimeter of film thickness. Thus, for the water-alcohol mixtures, the amount of iodine taken up by the polymer at equilibrium does not depend on the alcohol used, the molecular weight of the polymer, or whether the film is attached or suspended.

Water

PMMA is generally hydrophobic, and only small amounts of water ($< 1\%$) are absorbed into the poly-

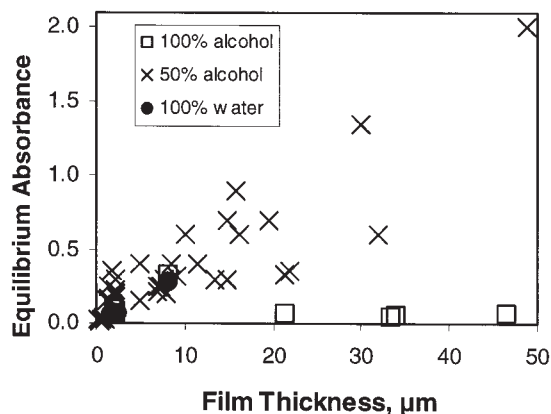


Figure 3 Equilibrium absorbance for various PMMA films in different solvents. No significant differences were seen for different molecular weights, between methanol and ethanol, or between attached versus suspended films. Films soaked in either 50% alcohol solutions or pure water fell along one line, while films soaked in undiluted alcohol fell along a different line. Additional measurements on thicker films ($\sim 100 \mu\text{m}$) in undiluted alcohol solutions also showed very low absorbance.

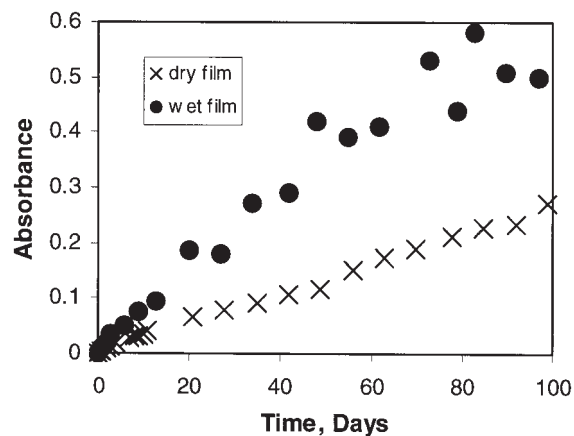


Figure 4 Change in absorbance of PMMA films ($\sim 15 \mu\text{m}$ thick, $145,000 M_w$) attached to glass immersed in water stained with $0.005M$ iodine. \times , initially dry film. \bullet , film soaked in undyed water for 40 days before immersion in iodine solution.

mer.⁶ Dry PMMA films placed in iodine-stained water show a slow uptake of iodine (Fig. 4, \times). The small amount of iodine entering the film could be carried along by solvent diffusing into the polymer or could simply be due to iodine diffusing directly into the film, with no solvent participation. To check which was occurring, films were first soaked in unstained water and then transferred to iodine-stained water. A film that was presoaked for 4.5 days showed behavior identical to the dry film, but films that were presoaked for 40 days showed significantly faster uptake of iodine (Fig. 4, \bullet). This increase in rate after presoaking could only occur if water is indeed entering the polymer and swelling the polymer network.

Films soaked in water took much longer to reach equilibrium than films in water-alcohol mixtures, but the swelling times were directly proportional the film thicknesses, giving a solvent penetration rate of $0.13 \pm 0.04 \mu\text{m}/\text{day}$. After reaching equilibrium, films soaked in water showed the same relationship between absorbance and thickness as films soaked in water-alcohol mixtures (Fig. 3).

Undiluted alcohols

No measurement of attached films in undiluted alcohols could be obtained, as, on each attempt, the films tore and detached from the substrate after just a few measurements. Suspended films also had a tendency to tear or detach from the holders, but results were successfully obtained on a number of suspended films. Films in undiluted alcohols showed an initial rapid increase in absorbance, which then either stabilized or slowly *decreased* in absorbance over a period of several days (Fig. 5). The reason for this decrease is not clear.

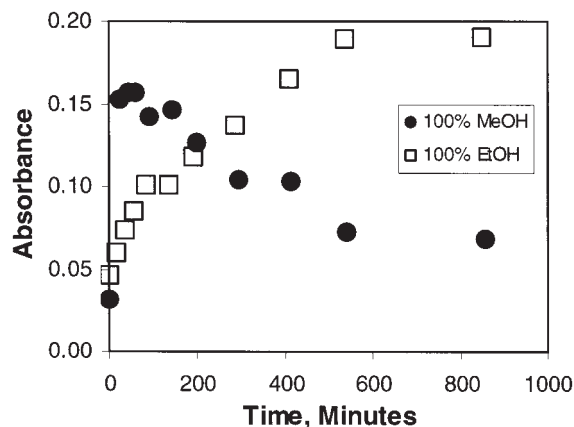


Figure 5 Change in absorbance of PMMA suspended films ($\sim 125 \mu\text{m}$ thick, $75,000 M_w$) soaked in solutions of iodine in undiluted alcohols. Absorbance was measured for a total of 12,000 min (9 days). After 1,000 min, the film in methanol showed a stable absorbance, while the absorbance of the film in ethanol fell slowly to about 0.1.

Swelling rates in undiluted alcohols showed much variation, and swelling times did not correlate to film thicknesses. Swelling rates in undiluted alcohols were much faster than rates in 50% alcohol, and, unlike the 50% alcohol results, in undiluted alcohols swelling was much faster in methanol than in ethanol. For comparison, the average solvent penetration rates were $2,850 \pm 3,100 \mu\text{m}/\text{day}$ in methanol and $400 \pm 400 \mu\text{m}/\text{day}$ in ethanol. The equilibrium absorbance of films soaked in undiluted alcohol was 1.6 per millimeter of film thickness, much less than the equilibrium absorbance of similar films soaked in alcohol-water or pure water solutions (Fig. 3).

Bulk samples

Pieces of sheet PMMA (Plexiglas, 4 mm thick) were immersed in dyed solutions of the undiluted alcohols and 50% alcohol in water. Plots of absorbance versus time (Fig. 6) were linear for 50% and undiluted ethanol and showed slight curvature for 50% and undiluted methanol. Swelling was greatest with undiluted methanol, and this was the only solution that caused visible swelling of the sample over a relatively short time scale (~ 10 days). At each time, the amount of solvent penetration on each side of the sheet could be found by measuring the unswelled central portion of the sheet, subtracting this value from the initial sheet thickness, and dividing by two. The measured solvent penetration rate for undiluted methanol was $130 \pm 15 \mu\text{m}/\text{day}$. In separate experiments, when PMMA sheet was sealed in a jar with dyed solvent for longer periods, the solvent penetration rate for undiluted ethanol was found to be $2.1 \pm 0.1 \mu\text{m}/\text{day}$.

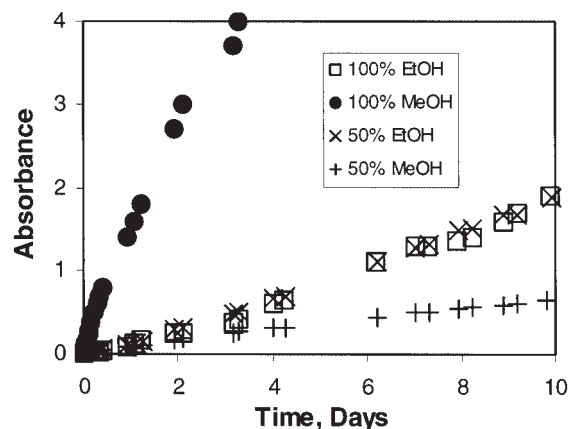


Figure 6 Change in absorbance of sheet PMMA (4 mm thick) in 0.005M iodine solutions. Change in absorbance for ethanol solutions is linear, $A \sim t$, while change in absorbance for methanol solutions is slightly nonlinear, $A \sim t^{0.8}$.

In Figure 6 it appears that 50% and undiluted ethanol swell the polymer at the same rate, but this is not necessarily the case. Thin films swelled by 50% alcohol had much greater linear absorptivities than thin films swelled by undiluted alcohols (Fig. 3, Table I), and the same may also be true of bulk samples. To test this, an independent measurement of the solvent penetration rate of 50% alcohol in bulk samples is needed, which is difficult because the penetration rates of 50% alcohol solutions are very slow. After 525 days in dyed 50% ethanol, sheet PMMA had a swelled layer $480 \mu\text{m}$ thick. Correction for swelling of the layer resulted in a solvent penetration rate of $0.8 \pm 0.1 \mu\text{m}/\text{day}$, which is significantly slower than the swelling rate for undiluted ethanol ($2.1 \pm 0.1 \mu\text{m}/\text{day}$). Thus, the apparent overlap between the 50% and undiluted ethanol measurements seen in Figure 6 is due to the sample in 50% ethanol swelling more slowly, but absorbing light more strongly. Similar measurements on sheet PMMA

TABLE I
Absorbance of Iodine in Solution and in PMMA after Soaking in Iodine Solution

Solvent	λ_{max} (nm)		Linear absorptivity (A/mm)	
	I ₂ in solution	I ₂ in PMMA	I ₂ in solution ^a	I ₂ in PMMA ^b
Water	355	385	11.9	35
50% Methanol	455	390	0.22	35
50% Ethanol	365	380	1.50	35
100% Methanol	450	380	0.33	1.6
100% Ethanol	365	370	1.53	1.6
100% Ethyl Acetate	460	—	0.24	—

^a Iodine concentration in all solutions 0.005M.

^b Iodine concentration in PMMA unknown.

in 50% methanol solution found a solvent penetration rate of $0.6 \pm 0.1 \mu\text{m}/\text{day}$.

Iodine absorption maxima

The color of iodine solutions is known to be solvent dependent. In noncomplexing solutions such as hydrocarbons, iodine is violet ($\lambda_{\text{max}} \sim 520$), while in complexing solutions such as alcohols, iodine is redish-brown ($\lambda_{\text{max}} \sim 470$).⁷ All of the iodine solutions used in this study had a similar yellow-brown appearance visually, but the exact position of the maxima varied (Table I). The absorption maxima of iodine adsorbed in PMMA varied slightly depending on the solution used, but to a much lesser extent than the variation in iodine absorption maxima in solution. Soaking PMMA in a violet solution of iodine in cyclohexane produced a similar yellow-brown color in the PMMA. For comparison, the absorption maxima of iodine was also measured in ethyl acetate (which is chemically similar to PMMA).

Absorption coefficients could not be calculated for iodine in PMMA, as the concentration of iodine is not known. For purposes of comparison, absorption was calculated as "linear absorptivity," or absorbance per millimeter of solution or unswelled polymer. Since the iodine in PMMA has a higher linear absorptivity than iodine in the solutions used (Table I), the concentration of iodine must be greater in PMMA than in solution or the iodine in PMMA must absorb more strongly than in solution (or both).

DISCUSSION

Polymer swelling is caused by solvent molecules diffusing into the polymer from solution. A solid polymer has very little free volume, so, in order for solvent molecules to enter the polymer, the polymer structure must relax and expand, creating the free volume for the solvent molecules to occupy. There are two limiting cases for solvent diffusion into polymers: Fickian and Case II, which differ in the relative rates of polymer relaxation and solvent diffusion.

In Fickian diffusion,⁸ the relaxation of the polymer is rapid compared to the diffusion of solvent through the polymer, and the concentration of solvent increases gradually and steadily from zero in unswelled regions to a maximum where the polymer is in contact with the solvent. As swelling progresses, the concentration gradient becomes more and more shallow, so the rate of solvent uptake (swelling) decreases with time. Fickian diffusion through a polymer is equivalent to diffusion through a viscous liquid.

In Case II diffusion,⁹ relaxation of the polymer is slow compared to diffusion of solvent through the polymer, and a sharp boundary exists between unswelled polymer and polymer that has been swelled to

nearly an equilibrium extent. Because the concentration gradient remains the same, only changing in position, the rate of solvent uptake (swelling) remains the same as swelling progresses.

Both types of diffusion can be described by the equation:

$$D = kt^N \quad (1)$$

where D is the diffusion, t is the time, and k and N are constants. For Case II diffusion, the amount of diffusion is linear with time and $N = 1$. For Fickian diffusion, the diffusion is initially rapid and slows with time and $N = 0.5$. The value of N can be determined from experimental data by taking the log of eq. (1):

$$\log(D) = N \log(kt) \quad (2)$$

So by plotting the log of the diffusion versus the log of the time, the slope of the plot will be the value of N , and discontinuities in the plot will indicate changes in diffusion mechanism.

Glassy polymers such as PMMA frequently show Case II diffusion in the bulk, and experimentally macroscopic (millimeter) PMMA shows Case II diffusion ($N = 1$) when swelled by alcohols near ambient temperature.^{1,5,10,11} As the temperature is increased, polymer relaxation becomes easier, and the swelling process becomes more Fickian. When PMMA is swelled by alcohols at elevated temperatures, the value of N is observed to decrease as the temperature increases, reaching 0.5 for swelling with methanol at about 60°C.^{1,5} Larger alcohols show similar behavior, but require higher temperatures to reach $N = 0.5$.¹⁰ Swelling of spin-coated PMMA films ($\sim 50 \mu\text{m}$ thick) has been studied by clamping the films between sheets of glass and exposing the film edge to solvent,¹² and swelling of these films by methanol was reported to be Fickian ($N = 0.5$) at room temperature. Solvent swelling of PMMA thin films ($\sim 0.3\text{--}3 \mu\text{m}$) measured by ellipsometry was found to be either Fickian or Case II depending on solvent and temperature.²

Plotting our results in log-log format frequently resulted in plots with three distinct sections: an initial section with $N \sim 0.1$, a middle section with $N = 0.5\text{--}1$, and a final section with $N \sim 0.3$ (Fig. 7). Most of the swelling occurred during the middle section, so this is the value of N that was used for analysis. All three segments were not observed in all experiments.

Our results for films in 50% alcohol solution are not clearly Case II or Fickian, but show some aspects of each. Values of N were near unity for some samples, and near one-half for other samples, while other samples had intermediate values. The variation in N did not correlate to film molecular weight, film thickness, or solvent used. Similar results were obtained with pure water and undiluted alcohols, although with al-

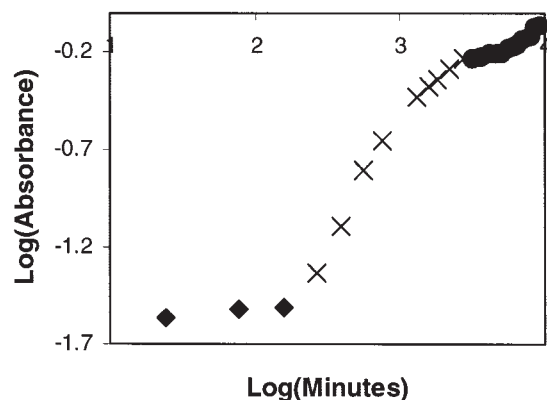


Figure 7 Log-log plot of swelling of PMMA (145,000 M_w , 16 μm , suspended film) in 50% ethanol. All points are from a continuous experiment; different symbols are used to distinguish the three regions of the plot. The first section (◆) shows little change in absorbance. The next section (×) shows rapid increase in absorbance (swelling), with a slope of about one in this case. The final section (●, upper right) shows a final very slow increase in absorbance.

cohols the swelling was often too rapid for good data to be obtained.

The sample-to-sample variation in N , and the shift toward Fickian diffusion relative to bulk samples, suggest that polymer relaxation in the films studied is both more rapid and more variable than relaxation in bulk samples of PMMA.

In experiments done with sheet PMMA (Fig. 6), swelling (measured by spectrophotometer) was Case II ($N \sim 1$) for 50% and undiluted ethanol and had a slight Fickian character ($N \sim 0.8$) for 50% and undiluted methanol. Swelling of sheet PMMA was also measured physically for undiluted ethanol and methanol and in both cases N was found to be ~ 1 .

Swelling rates

Although the absorbance-versus-time curves for films in 50% alcohol solutions do not show a clear endpoint (Figs. 1 and 2), an estimate of the time to reach equilibrium swelling was made for each sample. When these times were plotted against the film thicknesses, the points were very scattered, with no clear trend. This contradicts the commonsense expectation that thicker films will take longer to swell in solvent. Part of the reason for this lack of dependence on film thickness is likely the nonlinear nature of the swelling. Absorbance measurements frequently showed an initial slow increase followed by a period of rapid increase and a final period of slow increase to equilibrium (Figs. 2 and 7). If the initial and final segments are about the same for films of any thickness, then the only part that will depend on film thickness is the middle period of rapid increase, and so the total time would show little change with film thickness.

In pure water, swelling times were proportional to film thickness, with an average swelling rate of $0.13 \pm 0.04 \mu\text{m}/\text{day}$. No values of penetration rates for water in PMMA were found in the literature. Our attempts to measure swelling of sheet PMMA by water suggested a solvent penetration rate of $0.31 \pm 0.05 \mu\text{m}/\text{day}$, significantly faster than that observed for thin films. However, the "swelled region" observed for sheet PMMA in water dyed with iodine was very pale, while the swelled regions observed from 50% alcohol solutions dyed with iodine were quite dark. Results from thin films (Table I) suggest that the absorptivity per millimeter should be the same for water and for 50% alcohol solutions. Therefore, it is possible that the "swelled region" we observed for sheet PMMA in water was caused by a small amount of iodine diffusing into the polymer and that the actual swelled region was still too thin to measure.

For sheet PMMA in undiluted methanol the measured solvent penetration rate of $130 \pm 15 \mu\text{m}/\text{day}$ is similar to previously reported values of $130\text{--}170 \mu\text{m}/\text{day}$.^{1,2,5} The solvent penetration rate for undiluted ethanol was much lower: $2.1 \pm 0.1 \mu\text{m}/\text{day}$. The penetration rate for undiluted ethanol in PMMA at room temperature has not been reported but can be estimated from data presented by Andrews et al.⁶ at about $1 \mu\text{m}/\text{day}$, reasonably close to our result.

While no clear swelling rate could be measured for thin films in undiluted alcohols, since the swelling times were not proportional to the film thicknesses, the swelling rates were clearly much faster for thin films than for bulk samples and much faster than for thin films in 50% alcohol solutions. Our estimated solvent penetration rates of $2,850 \pm 3,100 \mu\text{m}/\text{day}$ for methanol, and $400 \pm 400 \mu\text{m}/\text{day}$ for ethanol are 20 and 200 times larger than the respective bulk values, but similar high swelling rates have previously been reported for thin films.

Morrissey et al.¹² measured edge-to-edge swelling of spin-coated PMMA films clamped between glass sheets and swelled in methanol. In contrast to bulk results, they observed Fickian diffusion ($N = 0.5$) and much higher swelling rates of approximately $1,000 \mu\text{m}/100 \text{ min}$ ($\sim 14,000 \mu\text{m}/\text{day}$). Durning et al.⁴ used interferometry to study swelling of thin PMMA films by methanol and measured a solvent front velocity of $0.059 \text{ mm}/\text{h}$ ($1,416 \mu\text{m}/\text{day}$). Stamatalis et al.¹³ studied edge swelling by methanol of clamped PMMA films and measured a swelling rate of $0.35 \mu\text{m}/\text{min}$ ($504 \mu\text{m}/\text{day}$).

The observed differences between bulk PMMA and spin-coated films could be due to the differences in molecular weight (bulk PMMA typically has an extremely high molecular weight) or to structural differences caused by the different methods of processing. The differences are probably not simply due to sample thickness, as Morrissey et al.'s results involved solvent

penetration across several millimeters of thin film. It is possible that stress relaxation at the solvent front occurs more readily in thin films than in bulk samples and that this contributes to the higher solvent penetration rates observed in thin films.

While the absolute values of solvent penetration in PMMA sheets and thin films were found to be quite different, the relative rates in both cases were the same: methanol > ethanol > 50% ethanol ~ 50% methanol > water.

Iodine absorbance

The λ_{\max} of iodine in solution depends on the solvent and varies by 100 nm between water, ethanol, methanol, and 50% alcohol solutions (Table I). After being adsorbed into PMMA, the λ_{\max} of iodine is different from that of any of the solutions and varies only slightly with the solution. When iodine dissolves to form yellow-brown solutions, the color results from the formation of complexes between the iodine and the solvent.⁷ Thus, the brownish color of iodine in PMMA is likely due to formation of a complex between iodine and PMMA. However, the precise nature of this complex is not clear. Ethyl acetate has similar functional groups to PMMA, but iodine dissolved in ethyl acetate does not show the same λ_{\max} as iodine adsorbed in PMMA (Table I). Taken together, these results indicate that 1) iodine is actively adsorbing to the polymer, and not simply being carried passively by the solvent, and 2) the complexation of iodine to PMMA is affected by the fact that PMMA is a polymer and is not simply due to interaction with specific functional groups.

Yellow-brown iodine solutions have been found to turn violet on heating, indicating a change from iodine complex ($\lambda_{\max} \sim 450$ nm) to free iodine ($\lambda_{\max} \sim 520$ nm).⁷ To see if a similar decomplexation could be accomplished with PMMA, thin (0.9 mm) PMMA sheets were soaked in methanol-iodine solution until fully swelled and then allowed to dry for 1 month. These sheets showed a very strong absorbance below ~ 500 nm (Fig. 8). When one of these iodine-stained PMMA sheets was heated on a hot plate, no color change was observed until the glass transition, at which point the sheet softened and also changed from yellow-brown to brownish-violet in color. On cooling, the sheets returned to a yellow-brown color visually very similar to the initial color. The transitory nature of the color change made it difficult to acquire spectra, but samples transferred to the spectrophotometer while still hot showed increased absorbance in the region near ~ 525 nm and greatly decreased absorbance near ~ 380 nm (Fig. 8). On full cooling, the absorbance above 500 nm returned to its initial value, but the decrease near 380 nm only slightly recovered. Subsequent cycles of heating and cooling simply cy-

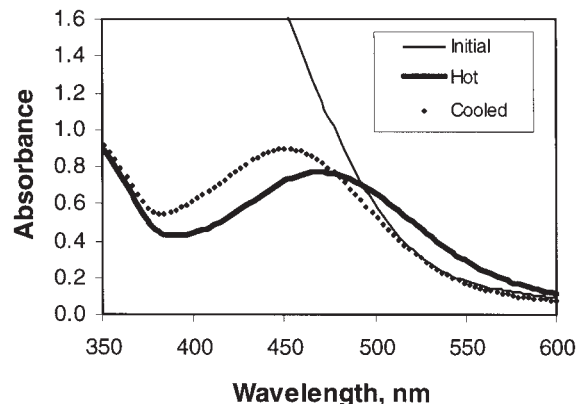


Figure 8 Absorption spectra of thin sheet PMMA (0.9 mm thick) swelled to completion in methanol-iodine solution and dried ("Initial"). Heating to the glass transition temperature produces a visual color change from yellow-brown toward violet, which fades on cooling.

led between the "hot" and "cooled" curves in Figure 8, with little additional change.

As was found for iodine complexes in solution, the PMMA-iodine complex also appears to break down at elevated temperatures, forming free iodine. On cooling, the PMMA-iodine complex forms again, but with greatly reduced absorptivity. This could be due to formation of a different type of complex or by loss or chemical reaction of some of the iodine. The fact that additional heating cycles do not cause additional loss in absorptivity suggests that the decline in absorbance is due to a change in the complex rather than to loss of iodine.

Swelling kinetics

The type of swelling observed (Fickian versus Case II) is determined by the competition between solvent diffusion and polymer network relaxation. Diffusion rates are mainly affected by temperature, while relaxation rates are affected by a number of polymer properties, for example, molecular weight and number of entanglements or crosslinks. Bulk PMMA samples have generally been found to exhibit Case II diffusion at room temperature, because the polymer relaxation is slower than solvent diffusion, but, at slightly above room temperature, polymer relaxation becomes more rapid and swelling moves toward Fickian behavior. The differences observed between spin-coated films and bulk samples are consistent with a reduced barrier to polymer relaxation in the spin-coated films compared to bulk samples. This could be due to lower molecular weight of the spin-coated films, to their lack of crosslinking, to trace amounts of residual solvent from the spin-coating process, to compacting of sheet PMMA during processing, or to thin films deforming more readily to accommodate stress relaxation at the

solvent front. Any or all of these factors could make polymer relaxation easier in the spin-coated films and make relaxation competitive with solvent diffusion at room temperature, which would put the films in the region between Fickian and Case II behavior, as was observed.

This spectrophotometric method for measuring solvent swelling of polymers is complementary to existing methods. While other methods work best with thick samples and solvents that cause rapid swelling, the spectrophotometric method is ideally suited for measuring slow processes in thin films. In addition, data analysis is straightforward, the method uses common laboratory equipment, and it is suitable for a wide variety of polymers and solvents. Undergraduate labs could use this method to study solvent swelling of polymers using the common "Spec 20" type spectrophotometer.

CONCLUSIONS

Spectrophotometry was successfully used to measure solvent swelling of thin polymer films by very poor solvents using a standard visible spectrophotometer. Swelling in the thin films differed from results previously reported from bulk polymer and was neither purely Fickian nor Case II. The difference is probably due to increased polymer chain mobility in the films, which allows polymer relaxation to compete with solvent diffusion. Iodine adsorbed into PMMA differed from iodine in solution both in absorption wavelength and in absorptivity. The increase in absorptivity led to

an amplification of the iodine absorption from poor solvents, greatly enhancing the value of the technique. Spectrophotometric measurement of swelling provides best results with thin films and very poor solvents, which are the situations in which traditional methods perform poorly. This method should be of great value in determining swelling for a variety of polymers and solvents.

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