Monitoring Water Uptake of Polyurethanes by *in Situ* Fluorescence Technique

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ABSTRACT: The water uptake of three polyurethane adhesives was studied by an *in situ* fluorescence method applying extrinsic fluorescent probes. The measurements were made in water immersion at 50 and 80°C, and in water vapor at 50°C. An intensity ratio method was applied, in which ratios of the highest and lowest intensity changes in the fluorescence emission bands were used to determine the amount of water sorbed in the polymer films. The ratio method was used to compare the fluorescence data with those obtained by a conventional gravimetric method. Comparable results were obtained. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1593–1599, 2001

Key words: fluorescence technique; water uptake; polyurethane polymer; *in situ* fluorescence

INTRODUCTION

The absorption of water causes many undesirable effects in adhesives. Even a small amount of water uptake in polymers and polymer adhesives can influence their properties by decreasing the glass-transition temperature and thus reducing the modulus. Traditionally FTIR,[1] NMR,[2] and dielectric measurements[3] are used to estimate the water content. Now the research interest centers on UV-Vis and fluorescence techniques. Extrinsic and intrinsic fluorophores have been successfully used for characterizing and *in situ* monitoring of water uptake, curing process, and oxidation in polymers.[4,5] The fluorescent molecular rotor probes have been used as extrinsic fluorescence sensors for quantitative monitoring of water uptake in polymeric protective coatings, polyamide-crosslinked epoxy coating, and poly(vinyl)ac-etate.[4] Extrinsic and intrinsic fluorescence approaches have also been made for monitoring water uptake in epoxy cured with a widely used aromatic diamine curing agent [diaminodiphenyl sulfone (DDS)].[5]

Fluorescent probes, which are sensitive to polarity or viscosity changes in their microenvironment, can be used to monitor the water uptake process. The basis for sensing the water uptake is that, in general, excited molecules are more polar and interact more strongly with the surrounding medium than ground-state molecules. When molecular rotor probes are used, the fluorescence intensity decreases as the adhesive absorbs water. The presence of water causes plasticization of the polymer, which increases the local mobility within the film; on the other hand, this increases the nonradiative decay pathways of the rotor probes and the resulting decrease in fluorescence intensity is directly proportional to the amount of water sorbed.[4]

In the present contribution the fluorescence method is used to study the water uptake of three polyurethanes. Most of the probes used in the present study are internal charge transfer (ICT)

Table I Configurations of Polyurethane Polymers

Polyurethane Type	Polyol Component (wt %)	Isocyanate Component (wt %)	Accelerator (wt %)
PU 1096	Polyether/polyester (58.7)	Hexamethylene diisocyanate (41.3)	Dibutyltin dilaurate (0.117)
PU 1391	Hexylenedyol (28)	Hexamethylene diisocyanate (72)	Dibutyltin dilaurate (0.05)
PU 1426	Polypropylene glycol (41.7)	Polyisocyanate (58.3)	Dibutyltin dilaurate (0.02)

compounds, containing both an electron donor and an electron acceptor moiety linked together by an aromatic chromophore. Because both rotation and charge separation are involved in the formation of the intermolecular charge transfer state, the fluorescence emission of the probe is sensitive to both the polarity and the microviscosity of the medium. The emission maxima of the probes shift to the red during the water uptake process as a result of the plasticization of the polymer matrix. Because of the increase in the local mobility within the film, the ICT probes form twisted conformers in the excited state emitting at longer wavelengths. When the polarity is changed because of the addition of water, fluorescence shows spectral shifts and the intensity decreases as a result of the alignment of the polar water in response to the increased dipole moment of the fluorophore in the singlet-excited state.[5] With the fluorescence technique measurements can be made *in situ* by using a fiber-optic fluorescence instrument and thus already small amounts of water can be detected.

EXPERIMENTAL

The components of three types of polyurethanes, type codes PU 1096, PU 1391, and PU 1426, were obtained from Gairesa Co., Spain. The component configurations are shown in Table I. The studied polyurethanes have an intrinsic fluorescence emission, although it is not suitable for monitoring the water uptake process. Thus, 13 fluorescent probes, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (4HP), 7-(dimethylamino)-4-(trifluoromethyl) coumarin (CO 152), ethyl 4-dimethylaminobenzoate (4EDMAB), *n*-(5-dimethylaminonaphthalene-1-sulfonyl)aziridine (DAZ), 8-anilino-1-naphthalene-sulfonic acid (ANSA), anthracene-9-carboxylic acid (9-AA) (Aldrich, Milwaukee, WI), 5-(dimethylamino)naphthalene-1-sulfonamide (DAM), 1,6-propionyl-2-dimethylaminonaphthalene (Prodan), 10,6-dode-

canoyl-2-dimethylaminonaphthalene (Laurdan), 7-hydroxy-4-methylcoumarin (7,4-CO), *n*-(5-dimethylaminonaphthalene-1-sulfonyl) hexadecylamine (DHDA), 5-dimethyl-amino-1-naphthalenesulfonic acid, monohydrate (DNSA) (Molecular Probes, Eugene, OR), and 4-dimethylamino-4′-nitrobiphenyl (DANBP) (Tokyo Casei), were tested for their suitability for monitoring the water uptake process of the polyurethanes.[6–10] All the probes were spectroscopic grade and used as received without further purification. The structures and abbreviations of the three selected probes are shown in Figure 1. Overlapping of the emission bands of the probe with the intrinsic emission of the polyurethanes or a weak emission intensity or quantum yield were the reasons for rejecting the other probes. The fluorescence emission spectrum was first measured from the dry sample, and after immersing the sample in water, in some cases, the emission peak of the probe disappeared. This could be attributed to the high temperature or diffusion of the probe molecules out of the polymer matrix. Probes behaving this way were rejected.

Homogeneous mixtures of the polyol component of the polyurethanes and the fluorescent
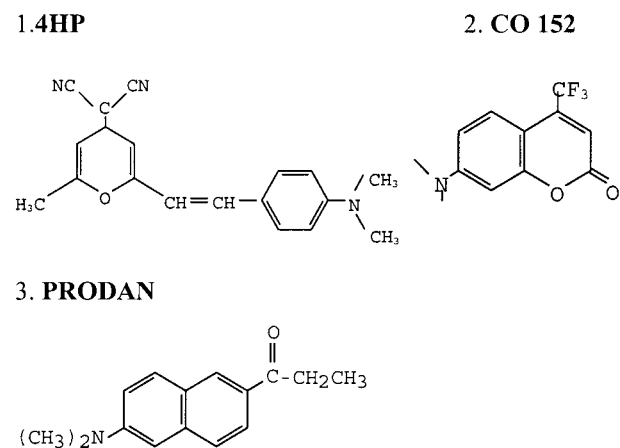

Figure 1 Structures and abbreviations of the fluorescent probes used to monitor the water uptake process.

probes (0.001 wt %) were made and the isocyanate component was added into the polyol–probe mixtures. The samples were cured for 1 week in a PTFE mold (thickness, 1 mm; width, 20 mm) inside a desiccator at room temperature.

In the gravimetric measurements the sample masses were recorded by the Precisa 205 A analytical balance. The samples were either immersed in water at 50 and 80°C, or kept in water vapor, 75% RH, at 50°C. The mass of the samples at different exposure times was measured to evaluate the diffusion coefficients. Fluorescence spectra were measured by a Spex Fluorolog 3 spectrofluorometer. By using a fiber-optic cable it was possible to monitor fluorescence emission *in situ*: the sample was adjusted in a holder and the excitation beam was focused on the sample with a lens.

RESULTS AND DISCUSSION

Diffusion in Polymers, Gravimetric

One of the most common experimental techniques for studying the diffusion of small molecules in polymers is the sorption kinetics method. If a plane polymer sheet is exposed to a fluid environment, the change of the concentration (C) of a diffusing substance as a function of time (t) and position (x) is given by the following expression of Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where D is the diffusion coefficient.

If the initial concentration of a penetrant is zero and if instantaneously after the polymer film has been placed in an infinite bath of the penetrant the two surfaces of the film ($x = L$ and $x = -L$) are established at a penetrant concentration C_s, the concentration at any position in the film of thickness (l) at any time is given by[11]

$$\frac{C}{C_s} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp[-D(2n+1)^2$$

$$\times \pi^2 t/l^2] \cos \frac{(2n+1)\pi x}{l} \qquad (2)$$

The sorbed mass is obtained by integrating eq. (2) over the thickness of the film:
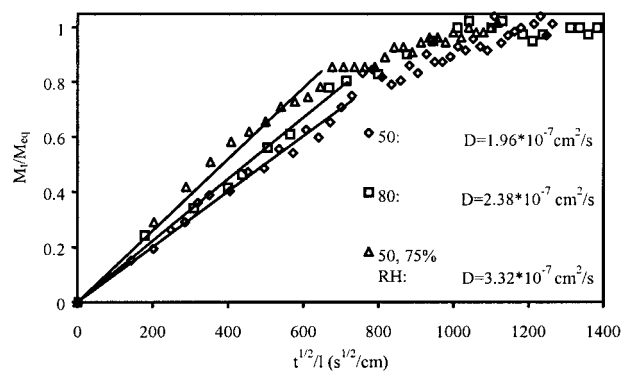

Figure 2 Mass uptake of PU 1096 in water immersion at 50 and 80°C, and water vapor 50°C (75% RH), as a function of $t^{1/2}/L$. The diffusion coefficients D are calculated from the initial slopes.

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{l^2}\right]$$

$$(3)$$

where M_t denotes the total amount of penetrant that has entered the film at time t, and M_{eq} denotes the amount at equilibrium.

One important Fickian sorption feature is that in the initial state both absorption and desorption curves are linear functions of $t^{1/2}$.[12] Thus, at short times, eq. (3) can be written as

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

The mass uptake (M_t/M_∞) of PU 1096 in three different environments as a function of $t^{1/2}$ is shown in Figure 2. For water absorption, the linear region extended out to a value of $M_t/M_\infty \leq 0.7$ for all three polyurethanes. Diffusion coefficients listed in the figure were determined from the initial slopes according to eq. (4).[13–15] For PU 1391 and PU 1426 similar dependencies were observed. The measurements were repeated and comparable results were obtained in all cases.

The samples made of PU 1391 and PU 1426 reacted very strongly with the air humidity, forming foamlike structures. The presence of air bubbles in the polymer matrix made it difficult to obtain good results from the gravimetric water immersion measurements. At 80°C the mass of some samples started to decrease after reaching the saturation level. This could be ascribed to the dissolution of the film in this condition. PU 1426
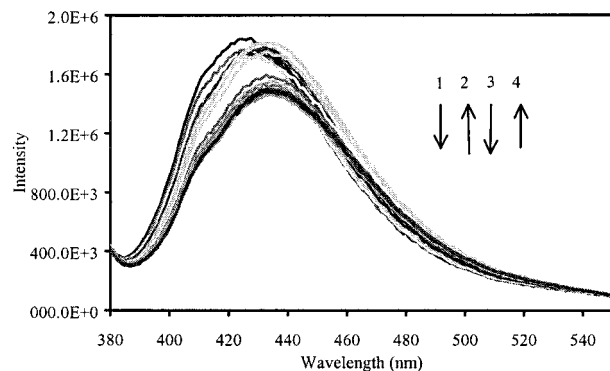
Figure 3 Fluorescence spectra of Prodan in PU 1096 immersed in water at 80°C. The arrows show the evolution of the spectra. The water uptake was followed for 150 min.

samples could not be measured at 80°C because of the deterioration of the film.

Water Uptake by Fluorescence

The emission spectra of the probe Prodan during the water uptake process of the PU 1096 in water immersion at 80°C are shown in Figure 3. The largest changes in the emission intensity were monitored in water immersion and at 80°C. In water immersion at 50°C and in 75% RH at 50°C, the changes, although quite small, could also be detected because of the sensitivity of the fluorescence method. The behavior of the probes depended on measuring conditions and on the polymer matrix. The fluorescence measurements were repeated and, despite the differences in external factors such as the sample thicknesses, similar results were obtained. A red shift of the emission maxima of the probes was observed in all cases, although the emission intensity changed irregularly. The emission maxima changes for each probe in the three polyurethanes are presented in Table II. The red shifts observed are only a few nanometers and indicate that the viscosity of the polymer matrix decreases and the polarity of the environment increases during the water uptake. Because of the small changes in the emission maxima they could not be used alone for monitoring the water uptake process.

In a previous study of monitoring the curing of polyurethane polymers by fluorescence we modified an LHIC (low-to-high intensity change) ratio method for analyzing the data.[16] This method is independent of both the type of polymer or probe

Table II   Wavelength Changes of the Emission Maxima of the Probes During the Water Uptake of Polyurethanes and the Wavelengths Chosen for LHIC Ratio Calculation

| Polyurethane Type	Probe	Wavelength Changes of the Emission Maxima During Water Uptake (nm)			Wavelengths Chosen for the LHIC Ratio (nm)		
		50°C	80°C	50°C, 75% RH	50°C	80°C	50°C, 75% RH
PU 1096	Prodan	5 $423 \rightarrow 428$	7 $427 \rightarrow 434$	1 $426 \rightarrow 427$	500/400	500/400	520/410
	CO 152	9 $455 \rightarrow 464$	8 $459 \rightarrow 467$	3 $454 \rightarrow 457$	530/430	560/430	550/430
	4HP	1 $567 \rightarrow 568$	11 $551 \rightarrow 562$	1 $555 \rightarrow 556$	660/500	630/530	620/530
PU 1391	Prodan	6 $427 \rightarrow 433$	13 $437 \rightarrow 450$	3 $430 \rightarrow 433$	500/430	500/430	500/400
	CO 152	0 $468 \rightarrow 468$	6 $467 \rightarrow 473$	3 $463 \rightarrow 466$	510/430	550/440	550/430
	4HP	7 $564 \rightarrow 571$	11 $566 \rightarrow 577$	4 $559 \rightarrow 563$	620/520	640/530	630/510
PU 1426	Prodan	6 $437 \rightarrow 443$	—	3 $438 \rightarrow 441$	480/420	—	520/420
	CO 152	0 $468 \rightarrow 468$	—	0 $473 \rightarrow 473$	550/445	—	520/440
	4HP	5 $572 \rightarrow 577$	—	1 $574 \rightarrow 575$	640/540	—	640/540
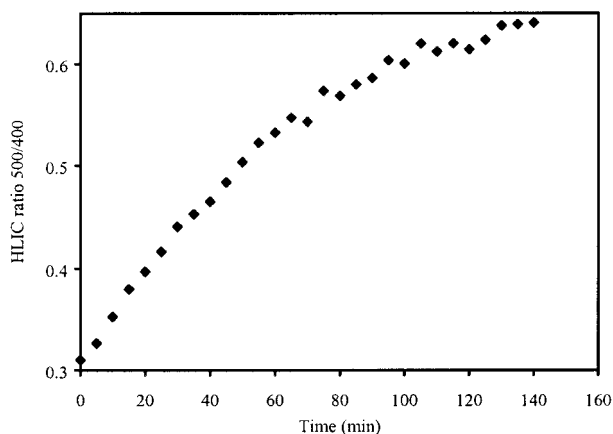
Figure 4 HLIC ratio as a function of time for Prodan in PU 1096 at 80°C.

and the experimental conditions. For the curing process blue shifts of the fluorescence emission maxima were observed, whereas for the water uptake red shifts were observed. Thus, instead of the LHIC ratio an HLIC (high-to-low intensity change) ratio should be used. In this method the final spectrum, measured at $t = \infty$, is divided by the initial spectrum, measured at $t = 0$, and the intensity changes are presented as a function of the wavelength. Thus, the wavelengths of the high-intensity changes (HIC) and the low-intensity changes (LIC) can be found. These wavelengths cover certain wavelength areas. This can be seen from Table II, where the wavelengths, which were chosen for applying the HLIC ratio method for each probe and polyurethane, are listed. The ratio of the HIC and LIC, the HLIC ratio, is then plotted as a function of time. As an example the HLIC ratio for Prodan in PU 1096 is presented in Figure 4.

Given that the changes in the fluorescence intensities are directly proportional to the amount of water sorbed, Fick's second law of diffusion[11] can be written as

$$\frac{M_t}{M_\infty} = \frac{I_t - I_0}{I_{eq} - I_0} = \frac{4}{l}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \tag{5}$$

where I_t, I_0, and I_{eq} denote the HLIC ratio at time t, 0, and ∞, respectively.

Figures 5, 6, and 7 present plots of both the relative mass uptake and relative fluorescence data of three different probes as a function of sorption times. These results indicate that the HLIC ratio method provides similar behavior for

the different probes in the same environment and the same experimental conditions. A good correlation is found between the fluorescence and the gravimetric data.

The fluorescence intensity change plotted as a function of the water mass uptake of PU 1096 at
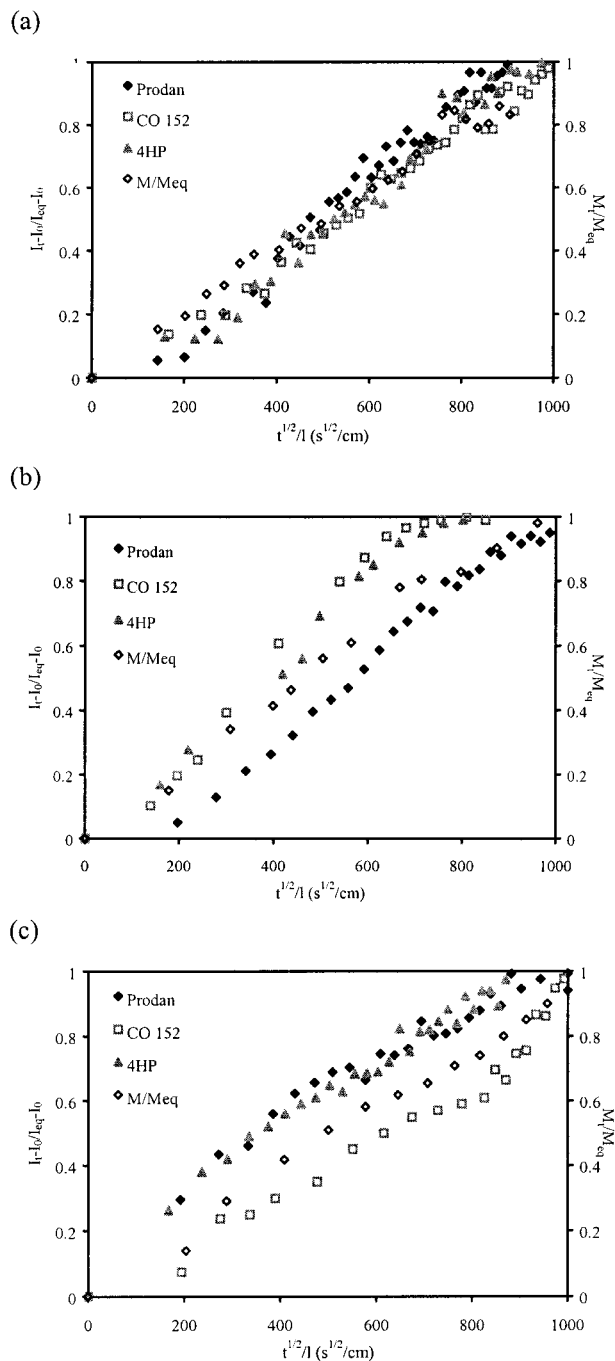
(a)

(b)

(c)

Figure 5 Intensity change of the three probes and mass uptake as a function of various sorption times for PU 1096 at (a) 50°C, (b) 80°C, and (c) 50°C, 75% RH.
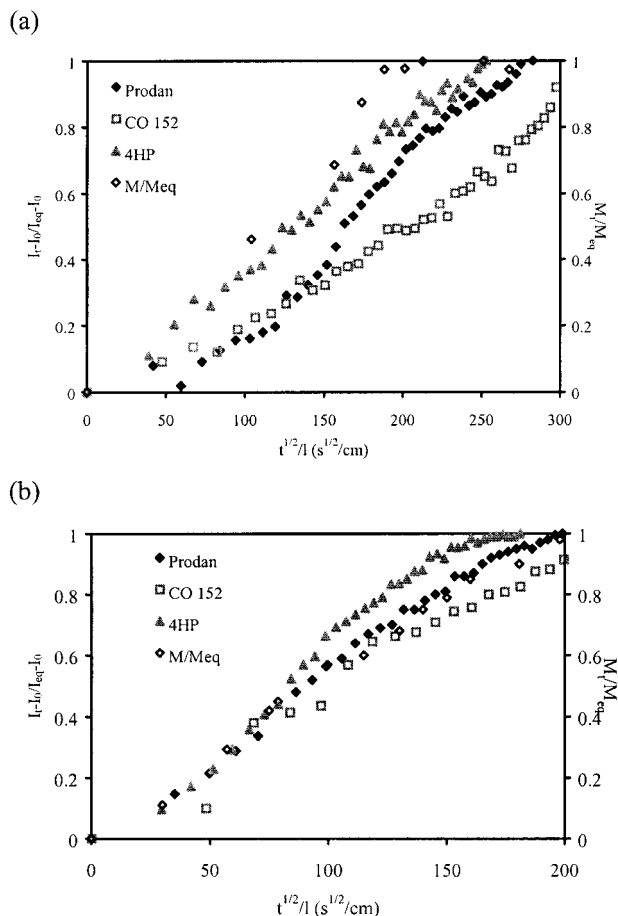
(a)

(b)

Figure 6 Intensity change of the three probes and mass uptake as a function of various sorption times for PU 1391 at (a) 50°C and (b) 80°C.
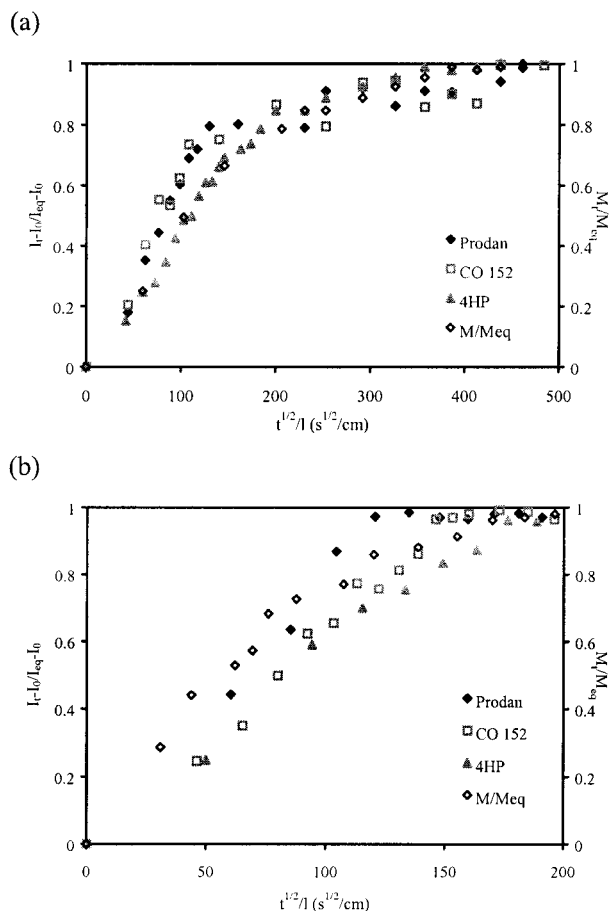
(a)

(b)

Figure 7 Intensity change of the three probes and mass uptake as a function of various sorption times for PU 1426 at (a) 50°C and (b) 50°C, 75% RH.

50°C is shown in Figure 8. A good one-to-one correlation between relative water uptake and the relative intensity change is obtained for all three probes. PU 1096 showed a linear correlation in all measuring conditions, whereas for PU 1391 and PU 1426 the correlation was not as good because of the presence of air bubbles in the samples.

According to eq. (5) the diffusion coefficients D can be calculated from the fluorescence data. For PU 1096 the correlation between the values of D obtained by the gravimetric method (slope, 0.0011; $D = 2.38 \times 10^{-7}$ cm²/s) and the fluorescence method (Prodan: slope, 0.0012, $D = 2.82 \times 10^{-7}$ cm²/s; CO 152: slope, 0.0011, $D = 2.38 \times 10^{-7}$ cm²/s, 4HP: slope, 0.0017, $D = 5.67 \times 10^{-7}$ cm²/s) at 80°C is quite good. For the other systems the correlation between calculated D values was less satisfactory because of defects in the polymer films.

CONCLUSIONS

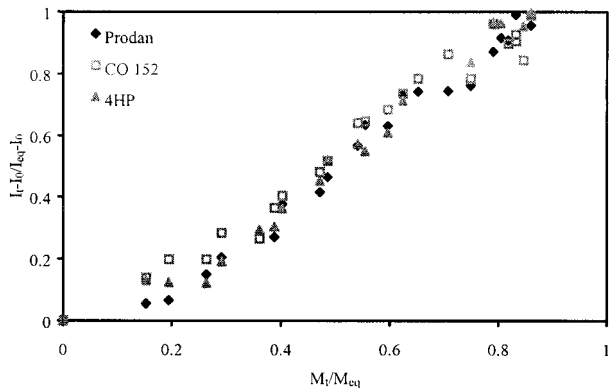Fluorescence spectroscopy was successfully applied for monitoring water uptake of polyure-

Figure 8 Intensity change of three different probes as a function of water mass uptake of PU 1096 at 50°C.

thane polymers. The influence of small changes in the experimental conditions, such as variation of temperature, relative humidity, thickness of the film, distribution of the probe in the polymer matrix, and diffusion of the probe into the surface of the polymer matrix, were all avoided by applying the HLIC ratio method. A regular correlation between the fluorescence intensity ratios, selected from the wavelength areas representing the highest and the lowest intensity change (HLIC), and the amount of water absorbed by the polymer film was obtained. This method provides a sensing technique that can be applied *in situ* for monitoring water uptake in a variety of commercially and industrially used polymers because it is independent not only of the type of probe but also of experimental conditions.

REFERENCES

1. Hartauer, K. J.; Matheson, L. E.; Guillory, J. K. Appl Spectrosc 1988, 42, 699.
2. Moy, P.; Karasz, F. E. Polym Eng Sci 1980, 20, 315.
3. Johnson, G. E.; Bair, H. E.; Matsuoka, S.; Anderson, E. W.; Scott, J. E. in Water in Polymers, Rowland, S. P., Ed.; ACS Symposium Series 127; American Chemical Society: Washington, DC, 1980.
4. Miller, K. E.; Krueger, R. H.; Torkelson, J. M. in Proceedings of the Fourth World Congress on Coating Systems for Bridges and Steel Structures, St. Louis, MO, 1995.
5. Sung, C. S. P.; Sung, N. H. Mater Sci Eng 1993, A162, 241.
6. Paczkowski, J.; Neckers, D. C. Macromolecules 1991, 24, 3013.
7. Wang, J.; Song, J. C.; Bao, R.; Neckers, D. C. J Polym Sci Polym Phys Ed 1996, 34, 325.
8. Jager, W. F.; Volkers, A. A.; Neckers, D. C. Macromolecules 1995, 28, 8153.
9. Keeny, S. M.; Antonucci, J. M.; Wang, F. W.; Tesk, J. A. Polym Prepr (Am Chem Soc Div Polym Chem) 1992, 33, 524.
10. Jager, W. F.; Kudasheva, D.; Neckers, D. C. Macromolecules 1996, 29, 7351.
11. Crank, J. The Mathematics of Diffusion, 2nd ed.; Oxford University Press: New York, 1975.
12. Lim, B. S.; Nowick, A. S.; Lee, K.-W.; Viehbeck, A. J Polym Sci Part B Polym Phys 1993, 31, 545.
13. Maffezoli, A. M.; Peterson, L.; Seferis, J. C.; Kenny, J.; Nicolais, L. Polym Eng Sci 1993, 33, 75.
14. Fieldson, G. T.; Barbari, T. A. Polymer 1993, 34, 1146.
15. Okamoto, K.-I.; Tanihara, N.; Watanabe, H.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y.; Nakagawa, K. J Polym Sci Part B Polym Phys 1992, 30, 1223.
16. Vatanparast, R.; Li, S.; Hakala, K.; Lemmetyinen, H. Macromolecules 2000, 33, 438.