

# Fourier Transform NIR Study of Liquid Diffusion Processes in Nylon 11 Films: Comparison of Water with Alcohols

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The diffusion of different deuterium-labeled (OD) low-molecular-weight alcohols and D<sub>2</sub>O in Nylon 11 has been investigated by monitoring the NH/ND exchange in the polymer by Fourier transform near-infrared (FTNIR) spectroscopy. The results demonstrate that the diffusion process of the different penetrants is strongly controlled by their molecular structure and geometry. To characterize this phenomenon quantitatively, the diffusion coefficients for the different deuteration agents have been determined for Nylon 11. The rate of the diffusion was found to decrease with increasing size of alcohol. Furthermore, it could be shown that with this technique the less ordered regions of the polymer can be separated spectroscopically from the crystalline domains, which are not accessible for the isotopically labeled diffusants.

## Introduction

Nylons are characterized by their good thermal stability, flexibility, and mechanical properties. The physical properties of nylons depend on a series of factors, one of the most important being their ability to absorb small molecules such as water and alcohols. The absorbed molecules change the melting and glass transition temperatures of the nylons<sup>1</sup> and strongly influence their mechanical<sup>2</sup> and electrical<sup>3</sup> properties. The diffusion and transport of small molecules in nylons is of importance in many application areas such as food packaging, protective clothing, or separation membranes. Therefore, the measurement of the diffusion coefficient is crucial to a better understanding of the material transport mechanism.

A number of experimental techniques have been used to measure the diffusion coefficients of small molecules in a polymer film by monitoring either the release from, uptake into, or permeation through the polymeric material. Gravimetric techniques<sup>4,5</sup> are the most frequently used methods. With use of this technique, polymer samples are mounted on a quartz spring microbalance and the change in mass is recorded as a function of time. The recorded weight is corrected for buoyancy to obtain the mass of the sample. If a sensitive microbalance is

used, this technique can be very accurate for determining diffusion coefficients for gases and vapors. However, if the density of the liquid is close to the density of the polymer, correction for buoyancy leads to considerably less accurate values of the sorbed mass; therefore, the quartz spring microbalance cannot be used to determine diffusion coefficients for liquids. In this case, the “pat-and-weigh” technique<sup>6</sup> is applied. This technique involves immersing the polymer sample in the liquid penetrant and periodically removing the sample, blotting the surfaces to remove excess liquid, and then weighing the sample on a laboratory balance.

The main difficulties with semicrystalline polymers arise from the inhomogeneity of the medium in which diffusion takes place. Usually, the semicrystalline polymers are regarded as composite materials consisting of impermeable microcrystalline domains imbedded in a matrix of permeable amorphous substance. The diffusion of penetrant molecules in perfectly crystalline regions of the polymer is expected to be negligible<sup>7,8</sup> and the diffusion coefficient may be considered to be zero. In the amorphous regions, the diffusion follows basically the free-volume model proposed by Cohen.<sup>9</sup>

In recent years, a spectroscopic method such as FTIR spectroscopy has been developed to complement existing techniques, such as the gravimetric method. The FTIR approach has potential advantages for making measurements on multicomponents systems and for elucidating specific chemical interactions that may be occurring during the permeation process. For polymers with labile hydrogen atoms in NH or OH functionalities,

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the H/D isotope exchange (deuteration) in combination with infrared spectroscopy is a convenient method of determining the accessible regions.<sup>10–12</sup> This method is based on the fact that the deuteration takes place only in the amorphous regions; therefore, the proportion of the deuterated functional groups should be equal to the proportion of accessible volume. However, the use of transmission spectroscopy in the mid-infrared (MIR) region to measure sorption kinetics suffers from many of the same limitations that are inherent to the pat-and-weigh technique. Due to the very strong absorptivity of the absorption bands in the MIR region (4000–400 cm<sup>-1</sup>), only very thin films (≈10–20 μm) can be used. If the sample is too thin or the diffusion coefficient is too high, a significant amount of penetrant may desorb during the time the sample is not immersed. Therefore, the attenuated total reflection (ATR)<sup>6,13</sup> or photoacoustic technique<sup>14</sup> have been proposed for this purpose. In the present study, we would like to demonstrate that near-infrared transmission spectroscopy is an even better alternative for measuring the sorption kinetics of small molecules in situ. With this technique film specimens up to about 1-mm thickness can be investigated. In such cases the deuterium exchange is slow enough during the spectroscopic measurements and the sample handling is very simple.

In an attempt to better understand the state of order of Nylon 11 and its implication on the mechanical properties of this polymer, we have performed extensive diffusion experiments with Nylon 11 film specimens in D<sub>2</sub>O and in a series of OD-deuterated alcohols of different molecular size and geometry. To monitor the rate of diffusion, we exploited the NIR spectroscopic isotope effects due to the NH/ND exchange induced by the penetrating deuteration agents. The idea behind this investigation was, on one hand, the spectroscopic separation of the amorphous and crystalline regions of this semicrystalline polymer and, on the other hand, elucidation of the mobility of the penetrant in the polymeric matrix as a function of its molecular size and geometry. To this end we have determined the diffusion coefficients for the different deuteration agents in Nylon 11.

## Experimental Section

Nylon 11 films used in this project with a thickness ranging from 0.5 to 1 mm were obtained from IFP (Institut Français du Pétrole, Rueil-Malmaison, France). The DSC results showed that the films had a crystallinity of about 25%. The original film was cut into test specimens with dimensions of 40 × 4 mm<sup>2</sup>. The molecular structures of the different deuterated alcohols utilized as diffusants in this investigation are listed in Table 1. The deuteration agents are varied with the aim to systematically increase the size and additionally to compare the diffusion behavior of linear versus spherical structures. For a diffusion experiment, a Nylon 11 test specimen was immersed in 5 mL of the deuteration agent at selected temperature and NIR transmission spectra were recorded

**Table 1. Molecular Structures of the Different Deuteration Agents**

deuteration agents	molecular structure
D <sub>2</sub> O	
Methanol (OD)	
Ethanol (OD)	
n-Propanol (OD)	
n-Butanol (OD)	
n-Pentanol (OD)	
t-Butanol (OD)	
3-Ethyl-3-Pentanol (OD)	

before and in selected time intervals during the deuteration process.

The NIR spectra were measured on a FTIR/FTNIR spectrometer (Bruker IFS 88) equipped with a tungsten halogen source, a quartz beam splitter, and a liquid-nitrogen-cooled InSb detector. To improve the signal-to-noise ratio, 50 scans were co-added at a spectral resolution of 4 cm<sup>-1</sup>.

## Brief Theory

**Determination of Diffusion Coefficients.** The IR spectroscopic method of determination of sorption diffusivity into polymer films is well established and will only be summarized here for convenience.

Generally, the one-dimensional molecular diffusion in a polymer film with a constant diffusion coefficient can be described by the second Fickian law,<sup>15</sup>

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where  $c$  is the concentration of the penetrant and  $D$  is the diffusion coefficient.

If a polymer film is placed in an infinite bath of diffusant, it has been shown that under certain boundary conditions (neglecting the effects if there is diffusion at the edges of the film) the mass-transported liquid at time  $t$  can be expressed by<sup>15,16</sup>

$$\frac{M_t}{M_{\max}} = 4 \left[ \frac{D}{\pi} \right]^{0.5} \frac{t^{0.5}}{d} \quad (2)$$

where  $M_{\max}$  is the mass uptake at saturation,  $M_t$  is the mass uptake at time  $t$ ,  $d$  is the film thickness, and  $D$  is the diffusion coefficient. It has been demonstrated that, at  $M_t/M_{\max} \leq 0.5$ , the diffusion coefficient of the penetrant in the polymer can be derived according to<sup>26</sup>

$$D = \frac{\pi}{16} J_a^2 \quad (3)$$

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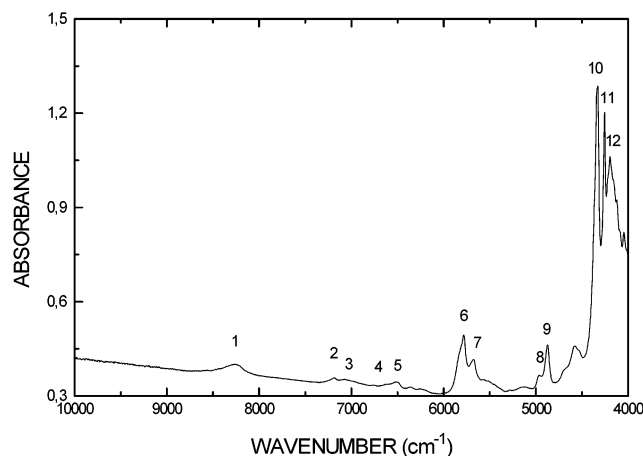
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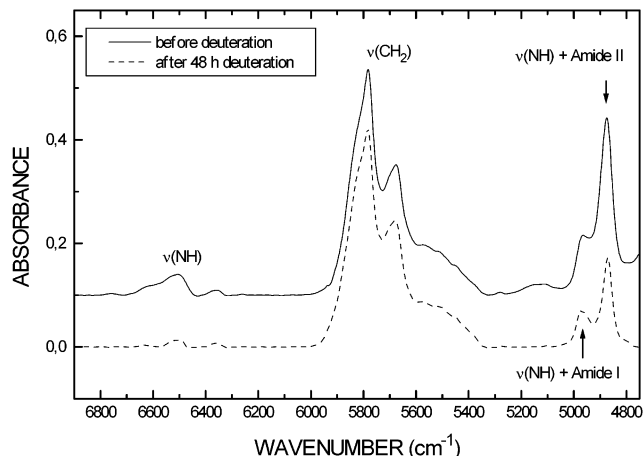
**Figure 1.** NIR spectrum of a Nylon 11 film (500  $\mu\text{m}$ , 27  $^{\circ}\text{C}$ ); the numbers correspond to the assignments in Table 2.

where  $I_a$  is the initial slope in a  $M_t/M_{\text{max}}$  versus  $t^{0.5}/d$  plot.

### Results and Discussion

Mid-infrared spectroscopy has been used extensively for the elucidation of the Nylon structure.<sup>12,17–19</sup> By comparison, spectra–structure correlations in the near-infrared region have received little attention and the band assignment for the NH group in the NIR region of the overtone (7000–6000  $\text{cm}^{-1}$ ) and combination bands (5000–4600  $\text{cm}^{-1}$ ) is not well understood yet.<sup>20–23</sup> The NIR spectrum of a Nylon 11 film (500  $\mu\text{m}$ ) in the wavenumber range 8000–4000  $\text{cm}^{-1}$  is shown in Figure 1. The absorption bands observed in this region and our assignments are summarized in Table 2. These assignments were verified by different techniques and investigations:<sup>24</sup> (1) relating fundamental vibrational frequencies of various structural groups in Nylon 11 to the frequency positions of possible overtone and combination bands; (2) interpreting the spectrum of partially deuterated Nylon 11; (3) taking into account the dichroic effects in spectra of stretched Nylon 11 films; (4) comparing spectra measured at different temperatures.

Figure 2 shows the NIR spectra of a Nylon 11 film (880  $\mu\text{m}$ ) before and after 48 h of deuteriation with *n*-propanol (OD). While the  $\nu(\text{CH}_2)$  absorptions at 5780 and 5680  $\text{cm}^{-1}$  are not affected by the deuteriation, significant intensity reductions upon deuteriation are reflected by those absorption bands that belong to vibrations involving the amide-hydrogen atoms. Thus, the weak band at 6760  $\text{cm}^{-1}$ , which has been assigned to the first overtone of the  $\nu(\text{NH})_f$  mode of the nonbonded NH functionalities (Table 2), has completely disap-



**Figure 2.** NIR spectrum of a Nylon 11 film (880  $\mu\text{m}$ ) in the wavenumber region 6800–4800  $\text{cm}^{-1}$  before and after 48 h of deuteriation with *n*-propanol (OD) at 50  $^{\circ}\text{C}$ .

**Table 2.** Assignment of the Absorption Bands in the NIR Spectrum (10000–4000  $\text{cm}^{-1}$ ) (See Also Figure 1) of Nylon 11 (f = Free, b = Bonded, as = Antisymmetric, s = Symmetric, w = Wagging)

	wavenumber ( $\text{cm}^{-1}$ )	intensity	tentative assignment
1	8265	m	$3^*\nu(\text{CH}_2)$
2	7184	m	$2^*\nu_{\text{as}}(\text{CH}_2) + \delta(\text{CH}_2)$
3	7070	m	$2^*\nu_{\text{s}}(\text{CH}_2) + \delta(\text{CH}_2)$
4	6760	w	$2^*\nu(\text{NH})_f$
5	6510	m	$2^*\nu(\text{NH})_b$
	6368	w	$\nu(\text{NH})_b + 2^*\text{amide II}$
	6256	w	$\nu(\text{NH})_b + \nu_{\text{as}}(\text{CH}_2)$
	6180	w	$\nu(\text{NH})_b + \nu_{\text{s}}(\text{CH}_2)_s$
6	5780	s	$2^*\nu_{\text{as}}(\text{CH}_2)$
7	5680	s	$2^*\nu_{\text{s}}(\text{CH}_2)$
8	4970	m	$\nu(\text{NH})_b + \text{amide I}$
9	4870	m	$\nu(\text{NH})_b + \text{amide II}$
	4706	m	$\text{amide I} + 2^*\text{amide II}$
	4586	m	$\nu(\text{NH})_b + \text{amide III}$
	4527	m	$2^*\text{amide I} + \text{amide III}$
10	4337	s	$\nu_{\text{s}}(\text{CH}_2) + \delta(\text{CH}_2)$
11	4258	s	$\nu_{\text{s}}(\text{CH}_2) + \delta(\text{CH}_2)$
12	4196	s	$\nu_{\text{s}}(\text{CH}_2) + \gamma_{\text{w}}(\text{CH}_2)$

peared. This fact indicates that the small percentage of NH groups that are not involved in hydrogen bonding is readily deuterated. Furthermore, the first overtone of the  $\nu(\text{NH})_b$  absorption of the bonded NH groups at 6510  $\text{cm}^{-1}$  and the two bands at 4970 and 4870  $\text{cm}^{-1}$ , which have been attributed to combination bands of the  $\nu(\text{NH})_b$  absorption and the amide I and amide II bands, respectively, were reduced in intensity after deuteriation. In Figure 3 the NIR spectra (5050–4750  $\text{cm}^{-1}$ ) of a Nylon 11 film (850  $\mu\text{m}$ ) deuteriated with ethanol (OD) are shown as a function of deuteriation time. From this figure it becomes clear that the intensity reduction for the 4970- $\text{cm}^{-1}$  band is much less significant than that for the 4870- $\text{cm}^{-1}$  band. The reason is that with progressing deuteriation the 4970- $\text{cm}^{-1}$  combination band is increasingly superimposed by the new  $2^*\nu(\text{ND})_b$  overtone.<sup>25</sup> In view of this overlap and the comparatively low intensity of the  $2^*\nu(\text{NH})_b$  overtone at 6510  $\text{cm}^{-1}$ , the isolated right wing of the 4870- $\text{cm}^{-1}$  band was utilized for the evaluation of the deuteriation progress as a function of time.

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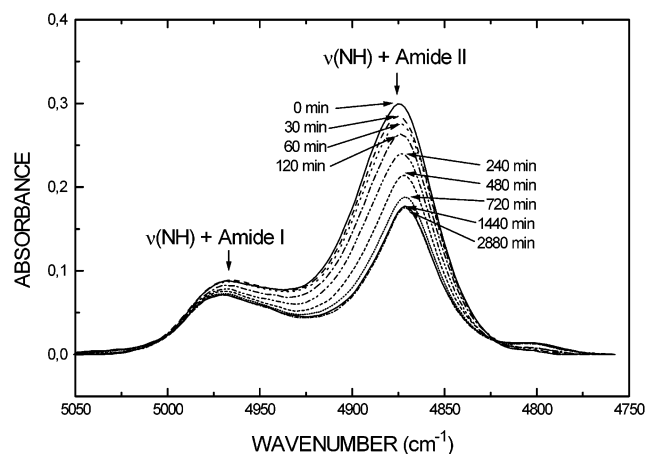
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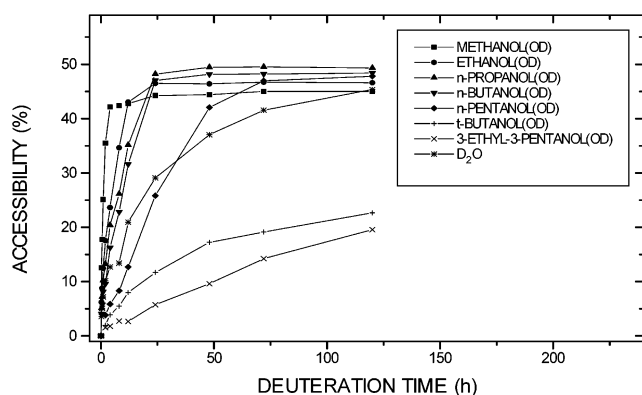
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**Figure 3.** Near-infrared spectra of a Nylon 11 film (850  $\mu\text{m}$ ) in the range 5050–4750  $\text{cm}^{-1}$  recorded in different time intervals during deuteration with ethanol (OD).



**Figure 4.** Progress in NH/ND exchange for the different deuteration agents.

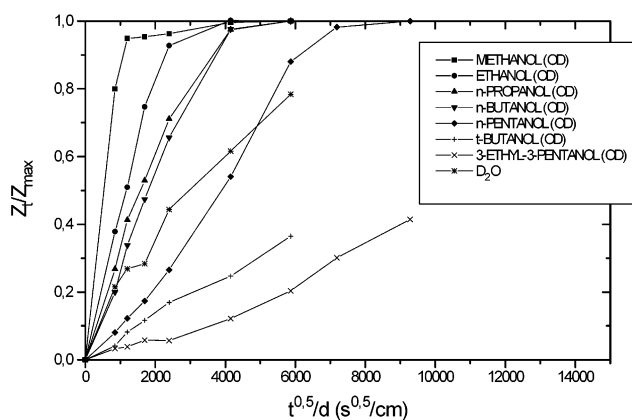
Generally, the accessibility of a Nylon 11 film in the deuteration process can be calculated quantitatively according to<sup>12</sup>

$$Z(\%) = \frac{A_{t=0}(\text{NH}) - A_t(\text{NH})}{A_{t=0}(\text{NH})} \times 100(\%) \quad (4)$$

where  $A_t(\text{NH})$  and  $A_{t=0}(\text{NH})$  are the absorbances of an NH-related band measured at deuteration time  $t$  and before the start of the deuteration, respectively.

The accessibilities of Nylon 11 for the different deuterating agents as a function of immersion time at 50 °C are shown in Figure 4. The graphics prove that the accessibility reaches a saturation level that is independent of the deuteration agent. Thus, after about 60 h of deuteration the linear alcohols (OD) have reached a plateau of about  $47 \pm 2\%$  accessibility. Only *tert*-butyl alcohol (OD), 3-ethyl-3-pentanol (OD), and  $\text{D}_2\text{O}$  have not reached their saturation level after this period due to their molecular size and their different structure, respectively.

The maximum accessibility of about 47%, however, is much lower than the amorphous fraction (about 75%) of the investigated Nylon 11 samples. Mukai<sup>26</sup> had shown that the amorphous fraction in polyamides can be categorized into two regions, conventional amorphous and rigid amorphous. The latter is located at the



**Figure 5.**  $Z_t/Z_{\text{max}}$  versus  $t^{0.5}/d$  plots for the investigated deuteration agents.

**Table 3.** Diffusion Coefficients of the Different Alcohols (OD) and  $\text{D}_2\text{O}$  for Nylon 11 (50 °C)

deuteration agent	diffusion coefficient ( $\text{cm}^2/\text{s}$ )
methanol (OD)	$1.74 \times 10^{-7}$
ethanol (OD)	$3.8 \times 10^{-8}$
<i>n</i> -propanol (OD)	$2.01 \times 10^{-8}$
<i>n</i> -butanol (OD)	$1.53 \times 10^{-8}$
<i>n</i> -pentanol (OD)	$2.41 \times 10^{-9}$
<i>t</i> -butanol (OD)	$9.22 \times 10^{-10}$
3-ethyl-3-pentanol (OD)	$2.96 \times 10^{-10}$
$\text{D}_2\text{O}$	$9.91 \times 10^{-9}$

interface between the amorphous and crystalline regions. At this interface, there are necessarily changes in density and chain mobility. These changes from a disordered amorphous state to an ordered crystalline state occur gradually. As a result, there exists a transition zone between amorphous and crystalline domains wherein the mobility of molecules is restricted compared with that in fully amorphous regions. Our deuteration experiments indicate that like the crystalline regions, the so-called rigid amorphous regions in nylons are not accessible for the deuteration agents at 50 °C.

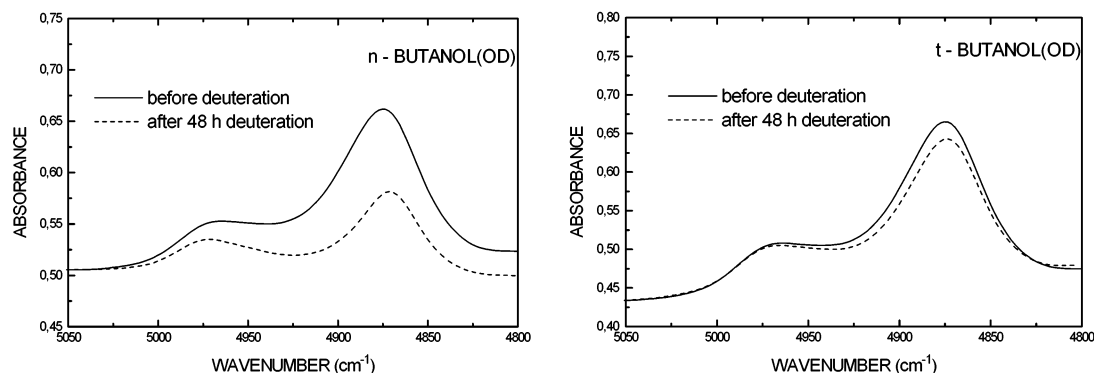
Because we have determined the accessibility by the progress of the NH/ND exchange instead of the mass uptake, the  $y$ -axis in our terminology reads  $Z_t/Z_{\text{max}}$ . The  $Z_t/Z_{\text{max}}$  versus  $t^{0.5}/d$  plots for the investigated deuteration agents are shown in Figure 5. The diffusion coefficients of the different deuteration agents calculated from these data according to eq 3 are given in Table 3.

When deuteration agents of the same type, for example, the linear alcohols (OD), are compared (Figure 4) with reference to the deuteration progress, an inverse relationship between the size of the diffusant and the deuteration rate could be derived. The same trend is observable for the alcohols with spherical structure (*tert*-butyl alcohol (OD) and 3-ethyl-3-pentanol (OD)). However, if deuteration agents of the same size but linear versus spherical geometry are compared, the alcohols with the spherical morphology exhibit a much slower deuteration progress (e.g., *tert*-butyl alcohol (OD)  $\ll$  *n*-butanol (OD) (Figure 6)). Obviously, the possibility for reptational motion<sup>27</sup> of the diffusant with a linear structure leads to a faster diffusion process.

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**Figure 6.** Comparison of the extent of NH/ND exchange with *n*-butanol (OD) and *tert*-butyl alcohol (OD) at equal deuteration time.

With reference to the slow and anomalous deuteration progress of Nylon 11 with D<sub>2</sub>O (Figure 4), however, it becomes obvious that the diffusive transport is not only governed by the molecular dimensions and geometry of the penetrant but other factors such as the polarity and especially the hydrogen bonding of the penetrating molecules play an important role. First, the deuterium bonding between D<sub>2</sub>O molecules is much stronger than that in the alcohols (OD). This is also reflected by the high boiling point (100 °C) of D<sub>2</sub>O compared to methanol (OD) (65 °C), ethanol (OD) (79 °C), and *n*-propanol (OD) (97 °C). Due to these stronger intermolecular forces in D<sub>2</sub>O, the molecules can associate to larger oligomers and thereby take on a spherical shape. Second, each D<sub>2</sub>O molecule can form two deuterium bonds with amide groups in the polyamide chain. Therefore, the D<sub>2</sub>O molecules are more strongly retarded in the polymer

matrix compared to the alcohols (OD), which can form only one deuterium bond.

### Conclusions

FTNIR spectroscopy has been successfully utilized to determine the diffusion coefficients of different alcohols (OD) and D<sub>2</sub>O in Nylon 11 by monitoring the NH/ND exchange in the polymer as a function of the immersion time. The results show that the amorphous regions of the polymer are not completely accessible to the diffusant and that the diffusion rate decreases with increasing molecular size of the penetrant. When deuteration agents of equivalent size are compared, linear species exhibit higher sorption rates relative to spherical moieties due to the possibility of reptational motion.

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