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The Diffusion of Acohols and Water in Polyamide 11: A Study by Fourier-transform Near-infrared Spectroscopy

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SUMMARY: The diffusion of different deuterium-labeled (OD) low-molecular-weight alcohols and D_2O in polyamide 11 (PA11) 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 PA11. 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

The diffusion of small molecules into polymeric materials is of importance in many areas such as food packaging, protective clothing or separation membranes. The physical properties of polyamides 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 polyamides1) and strongly influence their mechanical2) and electrical3) properties. Therefore, the measurement of the diffusion coefficient is crucial to both, a better unterstanding of the material transport mechanism and for the design of materials with optimized permeation properties.

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 4,5) are the most frequently used methods. Using 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,

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this technique can be very accurate to determine diffusion coefficients for gases and vapours. 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 can not be used to determine diffusion coefficients for liquids. In this case, the "pat-and-weigh" technique[6)] 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 semicristalline 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[7,8)] 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[9)]. For polymers with labile hydrogen atoms in NH- or OH-functionalities, the H/D isotope exchange (deuteration) in combination with infrared spectroscopy is a convenient method of determining the accessible regions[10-12)]. 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 (4000-400cm^{-1}), only very thin films (approximately 10-20μm) can be used. If the sample ist 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)[6,13)] or photoacoustic technique[14)] have been proposed for this purpose. In the present communication we would like to demonstrate, that near-infrared transmission spectroscopy is an even better alternative to measure the sorption kinetics of small molecules *in situ*. With this technique film specimens up to about 1mm 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 polyamide 11 and its implication on the mechanical properties of this polymer, we have performed extensive diffusion experiments with PA11 film specimens in D_2O 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 the one hand the spectroscopic separation of the amorphous and crystalline regions of this semicrystalline polymer, and on the other hand to elucidate 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 PA11.

Experimental

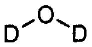
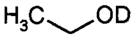
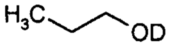
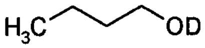
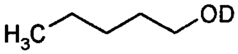
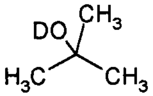
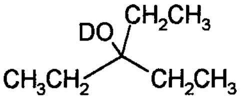
Polyamide 11 films with a thickness ranging from 0.5-1mm were obtained from IFP (Institut Francais du Petrole, Rueil-Malmaison, France). The DSC results showed that the films had a crystallinity of about 25%. The original film was cut into test specimens which were 40mm long and 4mm wide. The molecular structures of the different deuterated alcohols utilized as diffusants in this investigation are listed in Tab.1. The deuteration agents are varied with the aim to systematically increase the size and additionally to compare the diffusion behaviour of linear versus spherical structures. For a diffusion experiment, a PA11 test specimen was immersed in 5mL of the deuteration agent at 50°C and NIR transmission spectra were recorded 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. In order to improve the signal-to-noise ratio, 50 scans were coadded at a spectral resolution of 4cm^{-1}.

Results and discussion

Mid-infrared spectroscopy has been used extensively for the elucidation of the PA11 structure[12,15-17). By comparison, spectra-structure correlations in the near-infrared region have

Tab.1 The molecular structures of the different deuteration agents

DEUTERATION AGENTS	STRUCTURE
D_2O	
METHANOL(OD)	H_3C-OD
ETHANOL(OD)	
n - PROPANOL(OD)	
n - BUTANOL(OD)	
n - PENTANOL(OD)	
t - BUTANOL(OD)	
3 - ETHYL - 3 - PENTANOL(OD)	

received little attention and the band assignment for the NH-group in the NIR region of the overtone (7000-6000cm^{-1}) and combination bands (5000-4600cm^{-1}) is not well understood yet$^{18-21)}$. The NIR spectrum of a PA11 film (500μm) in the wavenumber range 8000-4000cm^{-1} is shown in Fig.1. The absorption bands observed in this region and our assignments are summarized in Tab.2. These assignments were verified by different techniques and investigations$^{22)}$:

--- relating fundamental vibrational frequencies of various structural groups in PA11 to the frequency positions of possible overtone and combination bands

--- interpreting the spectrum of partially deuterated PA11

--- taking into account the dichroic effects in spectra of stretched PA11 films

--- comparing spectra measured at different temperatures.

Figure 2 shows the NIR spectra of a PA11 film (880μm) before and after 48 hours of deuteration with n-propanol (OD). While the $\nu(CH_2)$ absorptions at 5780 and 5680cm^{-1} are not affected by the deuteration, significant intensity reductions upon deuteration are reflected by those absorption bands which belong to vibrations involving the amide-hydrogen atom. Thus, the weak band at 6760cm^{-1}, which has been assigned to the first overtone of the $\nu(NH)_f$ mode of the nonbonded NH-functionalities (Tab.2), has completely disappeared thereby indicating, that the small percentage of NH-groups which are not involved in hydrogen bonding are readily deuterated. Furthermore, the first overtone of the $\nu(NH)_b$ absorption of the bonded NH-groups at 6510 cm^{-1} and the two bands at 4970 and 4870cm^{-1}, which have been attributed to combination bands of the $\nu(NH)_b$ absorption and the Amide I and Amide II bands, respectively, were reduced in intensity after deuteration. In Fig.3 the NIR spectra (5050-4750cm^{-1}) of a PA11 film (850μm) deuterated with ethanol (OD) are shown as a function of deuteration time. From this figure it becomes clear that the intensity reduction for the 4970cm^{-1} band is much less significant than for the 4870cm^{-1} band. The reason is, that with progressing deuteration the 4970cm^{-1} combination band is increasingly superimposed by the new $2*\nu(ND)_b$ overtone$^{23)}$. In view of this overlap and the comparatively low intensity of the $2*\nu(NH)_b$ overtone at 6510cm^{-1}, the isolated right wing of the 4870cm^{-1} band was utilized for the evaluation of the deuteration progress as a function of time.

Tab.2. Assignment of the absorption bands in the NIR spectrum (10000- 4000cm^{-1}) of PA11 (f=free, b=bonded, as=antisymmetric, s=symmetric, w=wagging)(see also Fig.1)

	Wavenumber (cm^{-1})	intensity	tentative assignment
1	8265	m	$3*\nu(CH_2)$
2	7184	m	$2*\nu_{as}(CH_2) + \delta(CH_2)$
3	7070	m	$2*\nu_s(CH_2) + \delta(CH_2)$
4	6760	w	$2*\nu(NH)_f$
5	6510	m	$2*\nu(NH)_b$
	6368	w	$\nu(NH)_b$ + 2*Amide II
	6256	w	$\nu(NH)_b + \nu_{as}(CH_2)$
	6180	w	$\nu(NH)_b + \nu_s(CH_2)_s$
6	5780	s	$2*\nu_{as}(CH_2)$
7	5680	s	$2*\nu_s(CH_2)$
8	4970	m	$\nu(NH)_b$ + Amide I
9	4870	m	$\nu(NH)_b$ + Amide II
	4706	m	Amide I+2*Amid II
	4586	m	$\nu(NH)_b$ + Amide III
	4527	m	2*Amide I + Amide III
10	4337	s	$\nu_s(CH_2) + \delta(CH_2)$
11	4258	s	$\nu_s(CH_2) + \delta(CH_2)$
12	4196	s	$\nu_s(CH_2) + \gamma_w(CH_2)$

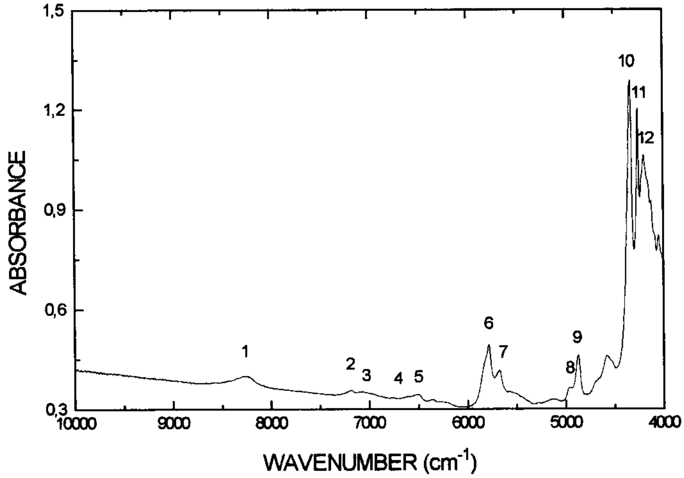


Fig.1: NIR spectrum of a PA11 film (500µm, 27°C; the numbers correspond to the assignments in Tab.2)

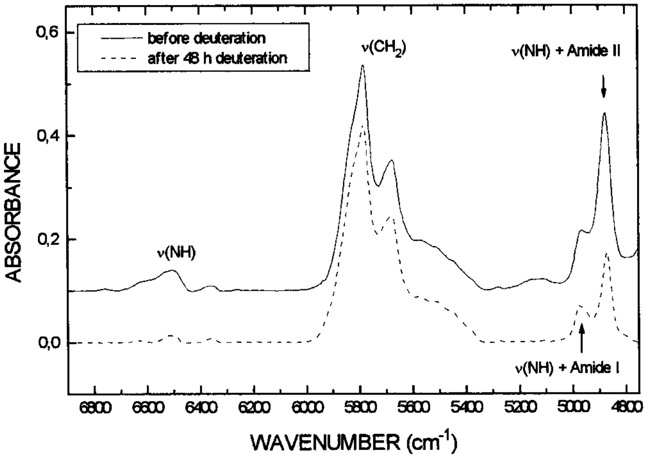


Fig.2: NIR spectrum of a PA11 film (880µm) in the wavenumber region 6800-4800cm^{-1} before and after 48 hours deuteration with n-propanol (OD) at 50°C

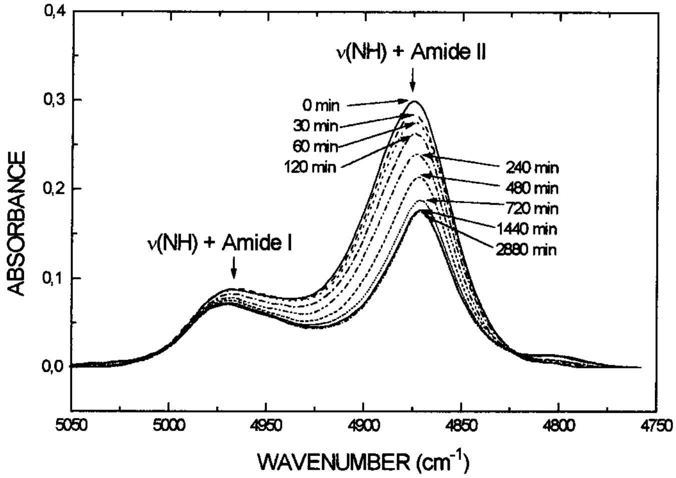


Fig.3: Near-infrared spectra of a PA11 film (850 μm) in the range 5050-4750cm^{-1} recorded in different time intervals during deuteration with ethanol (OD)

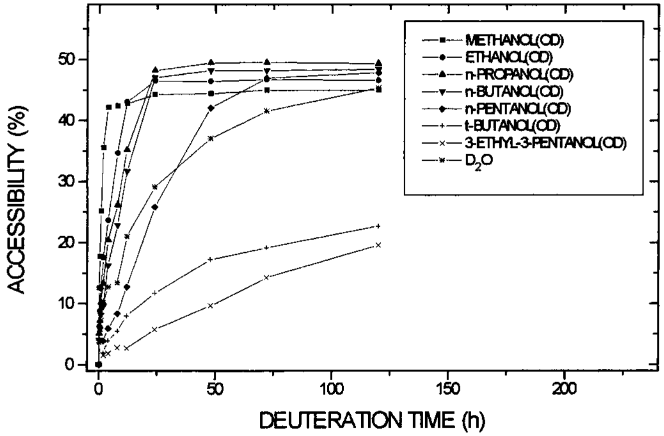


Fig.4: Progress in NH/ND-exchange for the different deuteration agents

Generally, the accessibility of a PA11 film in the deuteration process can be calculated quantitatively according to[12)]:

$$Z(\%) = \frac{A_{t=0}(NH) - A_t(NH)}{A_{t=0}(NH)} * 100(\%) \qquad \text{(Eq.1)}$$

where A_t (NH) and $A_{t=0}$(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 PA11 for the different deuterating agents as a function of immersion time at 50°C are shown in Fig.4. The graphs prove that the accessibility reaches a saturation level which is independent of the deuteration agent. Thus, after about 60 hours of deuteration the linear alcohols (OD) have reached a plateau of about 47±2 % accessibility. Only t-butanol (OD), 3-ethyl-3-pentanol (OD) and D_2O 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 PA11 samples. Mukai[24)] 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 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 polyamides are not accessible for the deuteration agents at 50°C.

When deuteration agents of the same type, e.g. the linear alcohols (OD), are compared (Fig.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 (t-butanol (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.

t-butanol (OD) << n-butanol (OD) (Fig.5)). Obviously, the possibility for reptational motion[25)] of the diffusant with a linear structure leads to a faster diffusion process.

With reference to the slow and anomalous deuteration progress of PA11 with D_2O (Fig.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_2O molecules is much stronger than that in the alcohols (OD). This is also reflected by the high boiling point (100°C) of D_2O compared to methanol (OD)(65°C), ethanol (OD)(79°C) and n-propanol (OD)(97°C). Due to these stronger intermolecular forces in D_2O, the molecules can associate to larger oligomers and thereby take on a spherical shape. Second, each D_2O molecule can form two deuterium bonds with amide groups in the polyamide chain. Therefore, the D_2O molecules are stronger retarded in the polymer matrix compared to the alcohols (OD) which can form only one deuterium bond.

Generally, the one-dimensional molecular diffusion in a polymer film with constant diffusion coefficient can be described by the second Fickian law[26)]:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad \text{(Eq. 2)}$$

where c ist 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 diffusion at the edges of the film) the sorption kinetics can be expressed by[26,27)]:

$$\frac{M_t}{M_{\max}} = 4\left[\frac{D}{\pi}\right]^{0.5}\frac{t^{0.5}}{d} \qquad \text{(Eq.3)}$$

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[26)]:

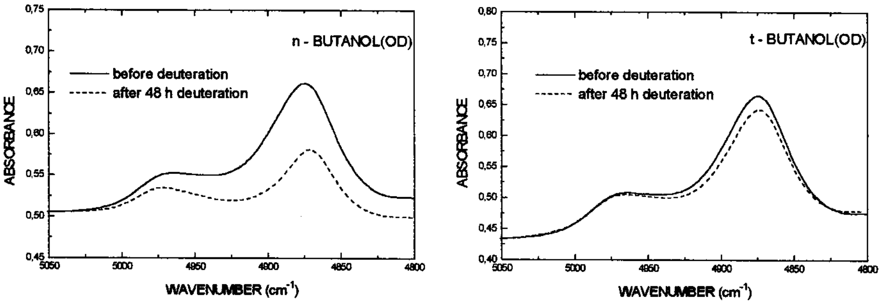


Fig.5: Comparison of the extent of NH/ND-exchange with n-butanol(OD) and t-butanol (OD) at equal deuteration time

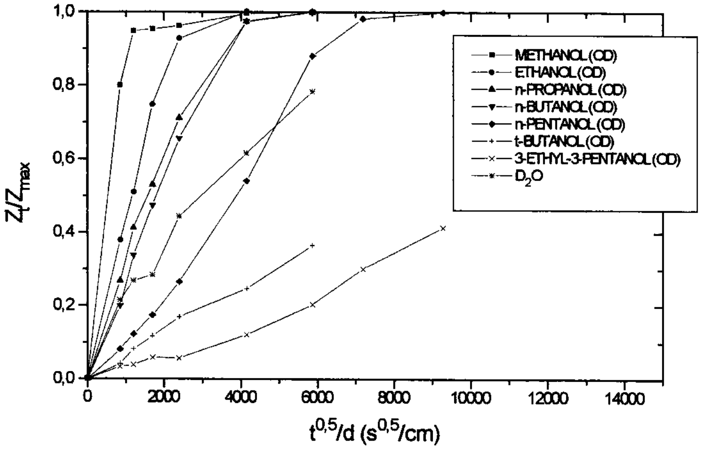


Fig.6: $Z_t/Z_{\max}$ versus $t^{0.5}/d$ plots for the investigated deuteration agents

Tab.3. The diffusion coefficients of the different alcohols (OD) and D_2O for PA 11 (50°C)

Deuteration Agent	Diffusion coefficient (cm^2/s)
METHANOL(OD)	$1,74*10^{-7}$
ETHANOL(OD)	$3,8*10^{-8}$
n -PROPANOL(OD)	$2,01*10^{-8}$
n -BUTANOL(OD)	$1,53*10^{-8}$
n -PENTANOL(OD)	$2,41*10^{-9}$
t -BUTANOL(OD)	$9,22*10^{-10}$
3 - ETHYL - PENTANOL(OD)	$2,96*10^{-10}$
D_2O	$9,91*10^{-9}$

$$D = \frac{\pi}{16} I_a^{\,2} \qquad \text{(Eq.4)}$$

where I_a is the initial slope in a $M_t/M_{\max}$ versus $t^{0.5}/d$ plot. 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 $Z_t/Z_{\max}$. The $Z_t/Z_{\max}$ versus $t^{0.5}/d$ plots for the investigated deuteration agents are shown in Fig.6. The diffusion coefficients of the different deuteration agents calculated from these data according to Eq.4 are given in Tab.3.

Conclusions

FTNIR spectroscopy has been successfully utilized to determine the diffusion coefficients of different alcohols (OD) and D_2O in polyamide 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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