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Investigation of Swelling and Diffusion in Polymers by NMR Imaging

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SUMMARY: The kinetics of diffusion in polymers ranges from simple Fickian diffusion to higher order diffusion, such as Case II diffusion[1-2]. The conventional method for determining the characteristics of solvents into polymer matrices is by measuring the mass uptake of the polymer as the solvent penetrates the matrix. However, since such measurements perform observations at a macroscopic level, little information has been obtained relating to the nature of the solvent in the polymer matrix and the mechanisms of the processes that control the diffusion. Nuclear magnetic resonance (NMR) imaging ('MRI') has been used to observe the penetration of solvents into solid systems in real-time. The method provides a one- or more-dimensional image of the density and the mobility of the solvent in a material or of the network changes of the material itself due to the softening influence of the solvent. The first (imaging of the solvent) can be used for a quantitative measurement of the diffusion whereas the observation of the network gives information about the changing of the network (mobility, de-crystallization...) during the swelling process. For example the diffusion of organic solvents in some polymeric materials (natural rubber, water gels (PNIPAAm), and nematic diblock-copolymers) are investigated.

Introduction

Due to a close interaction between the solvent and the polymer matrix the kinetics of diffusion in polymers ranges from simple Fickian (Case I) to higher order diffusion, such as Case II or non-Fickian diffusion[1-2]. In opposite to some conventional methods for the measurement of the diffusion process of solvents into polymer matrices (determination of the mass uptake, time lag method and others) MRI provides information relating to the nature of the diffusion process in the polymer matrix on a spatially resolved level with a resolution (voxel size) of c. 50...100µm. In this paper we give some examples both of case I diffusions in rubberlike material as well as anormal diffusion observed in water-gels at longer diffusion times and also an example of anisotropic diffusion processes, found in nematic LC-copolymers. The main feature of all these

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processes is the fact, that only a spatially resolved measurement method provides knowledge on the abnormal diffuison processes. For that the method of NMR-imaging (MRI) achieves success in the last decade[1,3-4]. For instance, these processes can be influenced by inhomogeneities such as surface layers (i.e. benzene in aged rubber[5]), polymer cracks, which allow a fast solvent uptake in relation to the matrix[1] or a change of the type of diffusion in some regions of the sample (i.e. water in PNIPAAm (Poly-N-isopropylacrylamide)[6]) and others. However, some experimental difficulties prevent a routine application until now. The reason is the large diversity of methods to obtain contrast in MRI: For an example, the contrast may arise from the solvent concentration itself which can be influenced by diffusion or convection. To specify the parameter (T_2, T_1, chemical shift or other) for observation a so-called filter sequence can be set before the imaging sequence is started. By this one can obtain images mainly showing the spin density of hydrogen atoms, the local mobility of a hydrogen atom (T_2-weighted by a multi-echo experiment), or a picture reflecting the diffusion and convection by using a simple Hahn-echo. On the other hand the contrast can also arise from the polymer matrix itself. In this case the diffusion process can be detected indirectly by measuring the changes of the polymer mobility due to the softening effects of the solvent. For both cases an example is given in this work.

NMR-Imaging of Diffusion

The basic principle of imaging, first introduced by P. C. Lauterbur in 1973[7], is the relation of a spatial coordinate (voxel) to a resonance frequency (see[8,9] for a more detailed description). This can be done by a magnetic field gradient G (Fig. 1), which shifts the frequency by

$$\omega_l = \gamma \cdot (H_0 + H_G) \; ;$$

(ω_l = resonance frequency of signal, γ = gyromagnetic ratio (in our case γ_H → gyromagnetic ratio for protons), H_0 = static magnetic field, and $H_G = r^* G$ = gradient field). :The Hahn echo pulse sequence for a one-dimensional imaging measurement used here is shown in Fig. 2. The magnetization in the xy-plane, created by a 90°-rf-pulse rotates in the laboratory system. Due to mainly dipolar interactions it dephases (loss of correlation) within a few ms (liquids) or µs (solids). The second pulse of 180° refocuses the magnetization to the echo signal at $2^*\tau$ which is acquired during the acquisiton (AQ) period. A Fourier transformation transforms the signal into the frequency space, which corresponds to the local dimension. For the image con-

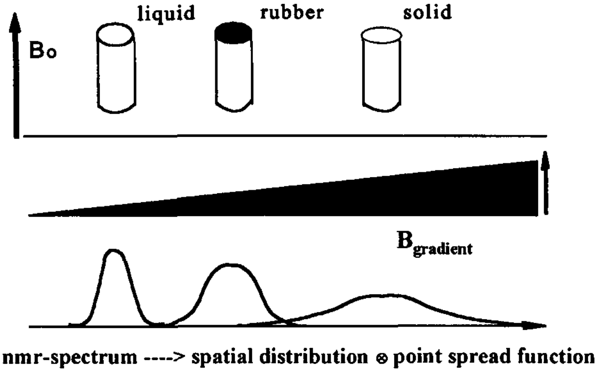


Fig1: The principle of NMR imaging: The spatial resolution is obtained by a magnetic field gradient, which shifts the resonance frequency of the spectrum. The non-averaged dipolar interaction in solid-like samples broadens the signal

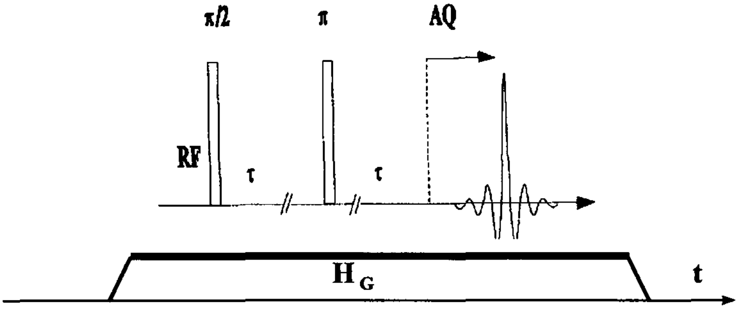


Fig.2: One dimensional imaging pulse sequence for a T_2-weighted (in dependence on the echo time τ) image. For other parameters (T_2, T_1, $T_{1\rho}$, ...) a so-called „filter sequence“ can be preset.

struction in the 2D- or 3D-case different mathematical procedures (Fourier Imaging, Back-Projection-Imaging) are used in dependence on the experimental situation (see[9] for a more detailed description). It is sketched in Fig. 1 that the resolution is not only determined by the gradient power but also strongly influenced by the dipolar linewidth (>2 kHz) and the chemical shift distribution (<1 kHz at υ_0 = 200 MHz) of a rubberlike material (e.g. natural rubber at

60°C) leading to a resolution of about $(100\mu m)^3$. For more liquid-like material (e.g. organic tissues) this can be reduced to $(20\mu m)^3$.

The measurements were performed on a self-made NMR microscope (actively shielded gradient coils up to 5mT/cm) attached to a VARIAN unity 200 spectrometer. The 2D-images were processed by Fourier imaging with slice selection (c. 500µm slice thickness). The 1D-images were aquired by a simple Hahn-echo shown in Fig. 2

The T_2 parameter

To obtain some information about the nature of the material the method of „material parameter imaging“[10)] was used: The echo time is changed during multiple measurement to obtain a decay of the magnetization in time, which is only influenced by the dipolar interactions in the case of a Hahn echo. However, for liquids a pure exponential decay (stochastic interaction due to Brownian motion) can be observed and the determination of a T_2-parameter (decay time) is straight forward. Of course, if diffusion and/or convection occure they dominate the echo decay, if a gradient is used. (Principially it is possible to separate the influence of diffusion also in NMR imaging by special pulse sequences[9)].) On the other hand the Hahn echo decay of more solid-like substances like rubber networks (or other polymer matrices) is not an exponential decay. The relaxation time T_2 gives only a very rough estimation of the molecular mobility. Using a multicomponent fit-procedure for the first gaussian-like part of the echo decay delivers some values (anisotropy parameter as a measure of the crosslink density, part of intercrosslink chains...) which give more information of the polymer matrix than a pure one-exponential fit. However, for imaging of diffusion experiments in real time a parameter selective measurement can be (as in our examples shown below) too much time consuming and a simple T_2-weighted experiment (Fig.2) is preferred.

Diffusion of Organic Solvent in Aged Natural Rubber

To investigate the influence of an aged layer on diffusion (as an example for a macroscopic property), we measured diffusion profiles in a real time procedure: The aged (170°C in air for different times, cf. Fig. 4) rubber pieces were placed in a tube and the solvent (benzene-d_6) was spilled on. The pictures (Fig.4) show the profiles (abscissa) and the time course (ordinate).

The beginning (two minutes after the contact to the solvent) is on the top, and the end (after 30 min) of the measurement is on the bottom of each figure. The left side of Fig. 4 represents the upper side of Fig. 3 (which contact the solvent in the probe). The changes through the images can be explained as follows[10]: At shorter aging times (55 min, 100 min) an aged surface layer characterized by a longer T_2 (lower crosslink density) facilitates the diffusion (and swelling). At very long aging times crosslinking processes (caused by radicalic polymerisation in the presence of oxygen take place and a higher crosslink density prevents swelling, but not the diffusion because of a violet network structure (polymer breaks).

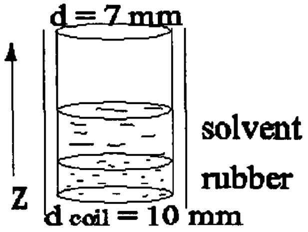


Fig.3 The NMR probe for the diffusion experiment: The rubber piece is aged on both (top and bottom) sides, but is covered by solvent only on the top.

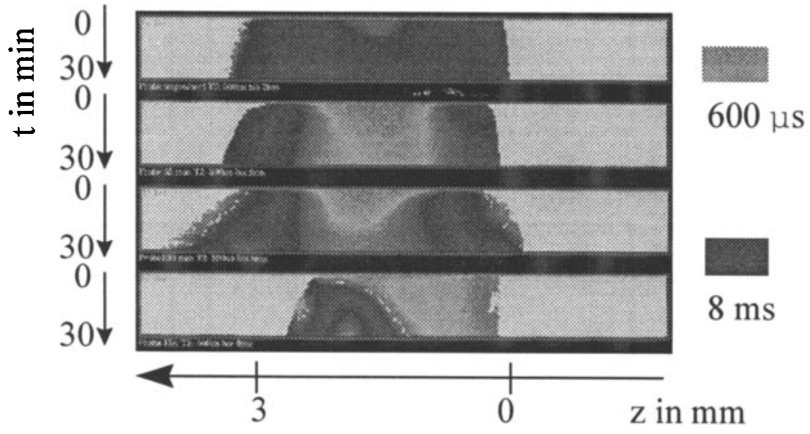


Fig.4:The diffusion in aged rubber shown by the T_2-parameter of the network. (The proton-free benzene-d_6 shows no signal.) The x-axis (local resolution) of this 1D-image corresponds to the z-axis in Fig.3. The thickness of the rubber pieces is about 3mm. The vertical axis of each picture is the time scale (top: 0min; bottom: 30min). Aging times: 1: unaged rubber; 2: 55min aged; 3: 100min aged; 4: 15h aged. The aging temperature was 170°C. The colour scale (here: grey scale by printing) for T_2 extends from 500μs (bright) to 8ms (dark).

Anisotropic Diffusion in Nematic Blockcopolymers (NBCP)

The prepolymer consists of statistically distributed segments of *tert*-butylhydrochinone, sebacic acid, 4-hydroxybenzoic acid and itaconic acid. The polymer was formed by a high-temperature solution polycondensation reaction in 1-chlo-ronaphtalene with *tert*-butylhydroquinone. The

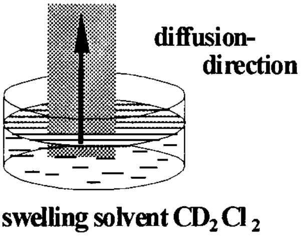
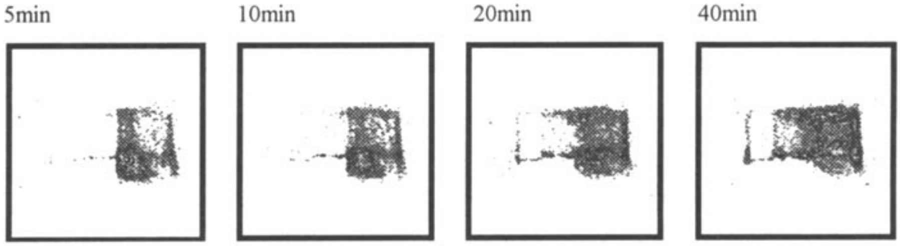
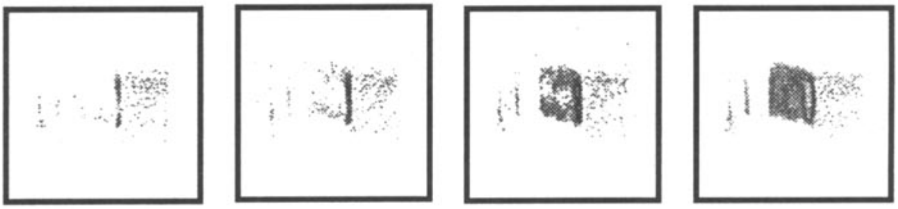


Fig. 5: Experimental set-up of the investigation of swelling of PES-MHC blockcopolymers



diffusion parallel to the preference direction



diffusion transverse to the preference direction

Fig. 6: Parallel and transverse diffusion of deuterated dichlorbenzene in an anisotrop nematic lc-blockcopolymer (PES-MHC). The figures are rotated at 90° in relation to experimental set-up. The bright vertical strip at 40min is the support device at the top of the polymer strip. Dark areas (originally coloured) show strongly swollen areas. The solvent uptake is influenced by adhesion effects.

crosslinking reaction proceeds via the double bond of the itaconic acid segments[11]. The anisotropy of this material (PES-MHC) was induced by mechanical stress during the cross-linking process ($M_c \sim 500000$ g/mol). It is known that the swelling behavior reflects very strongly the anisotropy of the polymer: The expansion ratio perpendicular to the orientation direction is more than 1.5 than that of the parallel direction at longer swelling times (>300min). By NMR-imaging of the diffusion fronts we focus our attention to anisotropies (of the velocities and intensities of the diffusion fronts) in the first stage of swelling (0 ...60min).

The diffusion of CD_2Cl_2 in PES-MHC takes place at room temperature. The experimental set-up inside the nmr-device is shown in Fig.5. The samples (c.3mm x 10mm) have a thickness of 1mm in the unswollen state. The immersion depth in the solvent was c. 1mm. The resolution of the T_2-weighted images (Fourier-Imaging at long (but fixed) echo time) is better than 100µm. Due to the fully deuterated solvent only the matrix protons of volumes already softened by the swelling process give strong signals. The unswelled parts show a more rigid lattice behavior including very short magnetization decays (short T_2) giving no or only a weak nmr-signal. The anisotropy of the diffusion is shown by

- the more effective overall diffusion of the parallel direction, which is pronounced by adhesion effects due to the macroscopic fibrous structure of the polymer. This structure diminishes the diffusion process in the transverse direction also.
- the more stepwise diffusion in the transverse direction (also a result of the fibrous structure).

Diffusion of a Methanol/Water-Solution in Water Gels (PNIPAAm)

PNIPAAm- (Poly-N- isopropylacrylamide) gels show some very interesting properties which offers some technical developments for the future (e.g. artificial muscle, temperature and pH sensitive switches):

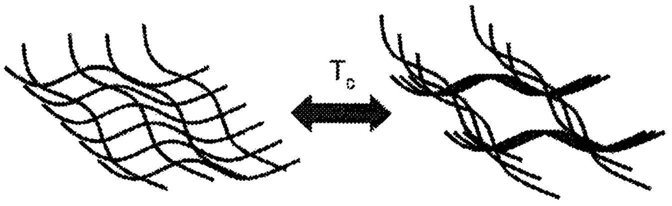
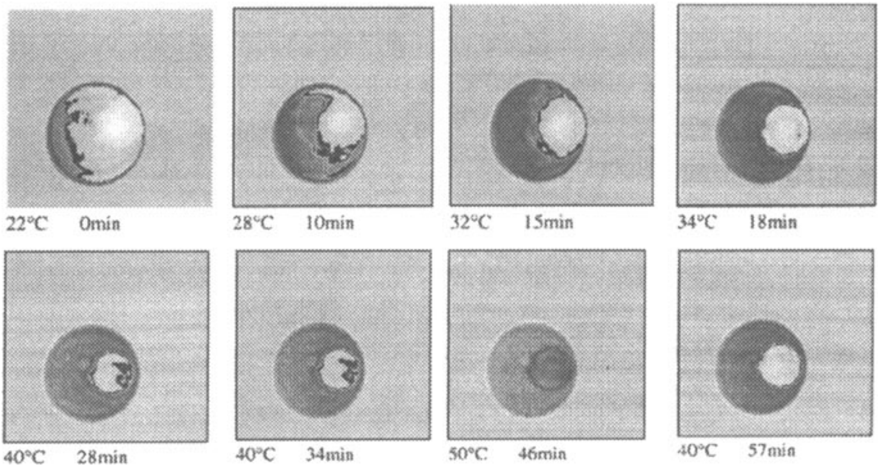


Fig. 7

- A volume phase transition temperature at T_{VPT} =34°C. The degree of swelling Q = $M_{swollen}/M_{dry}$ changes in dependence on the content of crosslinking agent (BIS) from up to 60 to about the 2 or less.
- The shrinking process shows a two step behavior: In a first period the polymer matrix changes to a more solid-like behavior by forming of macro network by bundles. (Fig.7) and without shrinking. However, after longer times the shrinking process takes place and the volume rapidly decreases.
- Tanaka et al[6)] could observe by PGSE-NMR, that also the diffusion constant (and also T_2 measured by a CPMG-sequence) of the water shows a rapidly decrease at the T_{VPT}.


22°C 0min
28°C 10min
32°C 15min
34°C 18min
40°C 28min
40°C 34min
50°C 46min
40°C 57min

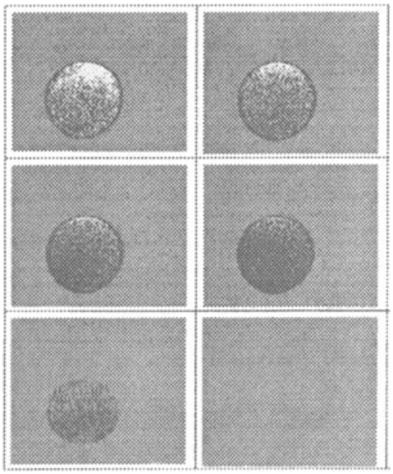


Fig. 8 and 9:
Deswelling behavior of PNIPAAm gel observed by Fourier Imaging in water (Fig. 8) and in deuterated water (Fig. 9).
(Fig. 9: 21°C, 25°C, 28°C, 30°C, 32°C, 34°C)
In both figures the inner diameter of the NMR-tube is 4mm and the slice thickness is c. 500µm. The image contrast arises from the T_2-weighted (diffusion!) spin density signal of the solvent (Fig. 8) and the polymer matrix (Fig. 9). The brighter the areas the longer the T_2 and the higher the mobility of the material.

- Also they could show the formation of a surface layer during the shrinkage process for highly-crosslinked gels by NMR-imaging.
- In dependence on the concentration of methanol in the swelling solution shrinkage occurs also at lower temperatures. The maximum effect is shown at c. 40 wt% methanol

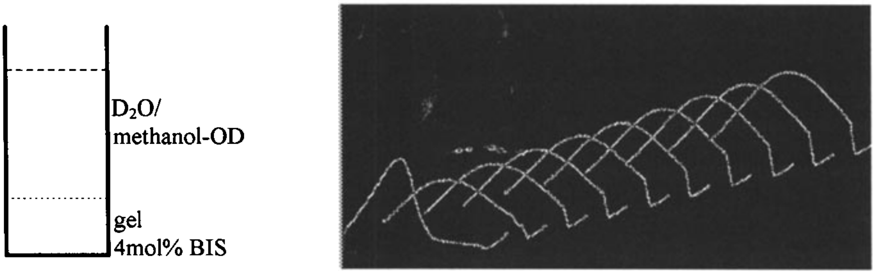


Fig. 10: one-dimensional diffusion experiment (60vol% methanol): left: experimental setup. right: MRI of ten equidistant time-steps (5min → 2600min, z-gradient only). The left side of each scan is the top volume (solution) of the experimental setup

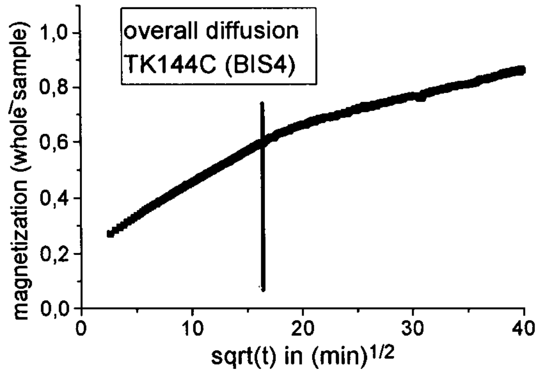


Fig. 11: Overall magnetization of the whole sample volume as a function of √t shows clearly Case I diffusion ($M_t \sim t^{1/2}$) for the first time period (0 → c. 300min). Here shown for the solution of 60vol%-methanol-OD as an example. (T(measurement)= 21°C)

We performed some NMR-imaging measurements to proof some of the statements given here. The samples were prepared by free radical polymerization of NIPAAm in water with different content (1...10mol%) of N,N'-Bismethylenacrylamide (BIS) as the crosslinking agent.

In Fig.8 the deswelling of a cylindrically shaped gel in water is shown by NMR imaging. 2D Fourier Imaging with slice selection (c. 500µm) was used to get T_2-weighted pictures. The inner diameter of the NMR-tube was 4mm. The best contrast of the gel in relation to the water is observed in the image after 18min at T_{VPT} due to the large difference in the mobility of the water in the gel and the surrounding volume. The shape and the area of the gel is nearly the same in all pictures (The bright surrounding areas in the figures at 22°C and 28°C is caused by a hindrance of convection nearby the surfaces of gel and tube.). The beginning of the shrinkage as the second step of the process is even later. This is in agreement with integral (non-imaging) NMR-measurements[6)], which show a rapid decrease of T_2 long before shrinkage takes place. However, some inhomogeneities at higher temperatures can be seen (black areas at 40°C). At 50°C the contrast decreases due to a decrease of T_2 of the immobilized water. A further hint of the two step behavior of the shrinkage process shows the image of the polymer matrix by replacing the water by deuterated water (Fig.9). At T_{VPT} the matrix vanishes due to the change of the network to a more solid-like (rigid lattice) material (T_2 decreases rapidly.).

The change in the swelling behavior by using a solution of D_2O/CH_3-OD (partially deuterated methanol) was also investigated by MRI. The methanol concentration varies from 0 (D_2O/H_2O) to 80vol%. In fig. 10 the experimental setup is shown. As a result it is shown that

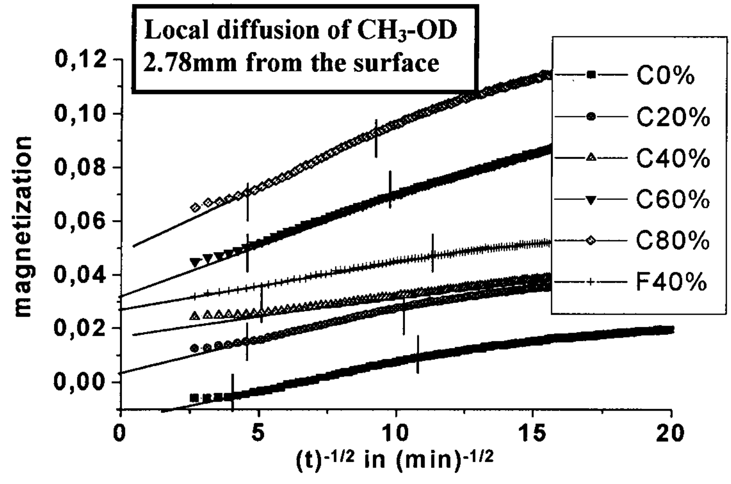


Fig.12: Magnetization as a measure of the methanol-OD concentration inside the gel at a distance of 2.78mm from the solution-body-surface of a PNIPAAm-gel (BIS 4) during the diffusion process ($t^{-1/2}$). The solutions are as follows: C0% -pure water, C20% - 20vol% methanol, ... C80% - 80vol% methanol, F40% - sample BIS10; 40vol% methanol. The first marks show the time lag and the second the end of the nearly linear dependence on $t^{-1/2}$.

the first period is Case I diffusion for all concentrations (including pure water). The conclusion is, that in the first period of diffusion (up to c. 300min at 21°C)) of methanol in the sample no change of the network occurs, which would be able to hinder the diffusionMRI is able to give information of a single local process in relation to other samples. In Fig. 12 the increase of magnetization of a thin sample layer (thickness c. 60µm) at 2.78mm distance to the surface as a measure of the methanol concentration for several experimental starting conditions is shown. The experimental setup is the same as shown in fig.10. The curves are represented in dependence on the square root of the time to pronounce the different sections of the diffusion process:

- The time lag depends slightly on the methanol concentration with a maximum at 40vol%. This reflects the shrinking minimum at this concentration (see above of this section). A rough estimation of the diffusion constant is possible using $D = l^2/(6*\Theta)$ (l=2.78mm; Θ= time lag) providing nearly the diffuison constant of free water (D_{water}= $2.3*10^{-3}mm^2/s$)12). The 40vol%methanol solution deviates slightly to longer times
- The end of the nearly linear part is almost the same for all concentrations except for the 40vol% one which shows a very delayed diffusion process. The highly-crosslinked sample (sF40 - BIS10) shows also a delayed diffusion behavior.

Another feature of the diffusion of methanol in a PNIPAAm gel is the formation of surface layers which delay or prevent further diffusion of the solvent. This was already observed6) for highly-crosslinked gels, but as an effect of the volume transition temperature in pure water. In fig. 13 it is also shown for the methanol diffusion at room temperature (21°C).

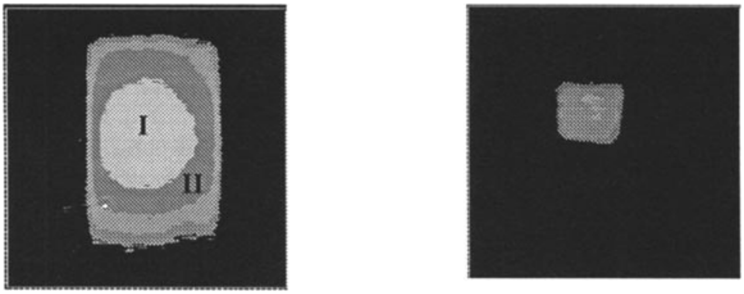


Fig.13: Fourier-Images (slice selection, T_2-weighted) of a vertical plane of two in 40vol% methanol solution deswollen PNIPAAm-gels after three days:
left: sample F (BIS 10) right: sample C (BIS 4)
Notice of the surface layer (II) of the F-sample, surrounding by solution. In the center is an unshrunked area (I) also after some days. In the case of sample C no surface layer and no unshrunked volume can be seen. At the beginning of the diffusion process the sample volumes were nearly equal.

Conclusions

The aim of this paper was to present some examples of MRI-investigations of diffusion processes. NMR-Imaging is a powerful tool for spatially resolved investigation of diffusion processes in polymeric networks in real-time conditions, however it is far from being a „routine application“ until now. In dependence on the material (rubber-like networks, polymer glasses, water gels) the matrix or the solvent can be observed by different NMR-parameters (T_2, T_1, qM_2...) which have to be chosen carefully for the different purposes

In relation to denser materials (rubber, plastics) the imaging of diffusion in gels is complicated by self diffusion (and convection) effects which dominate the magnetization decay.

For the gel materials shown here a case I diffusion for the beginning of the diffusion process is stated. For longer diffusion times and organic solvent parts (methanol) the process deviates from case I diffusion according to the network changes (Two step model of the deswelling process). The spatially resolved solvent uptake shows deviations already in the case I regime in relation to pure water at different methanol concentrations. This is a hint for network changing by the solvent agent also in the first period of case I diffusion. The otherwise observed features of the (de-)swelling behavior at methanol concentrations of c. 40vol% could be confirmed by MRI. The analysis of the concentration increase in thin layers at a fixed distance to the surface and the observation of a surface layer of hindered diffusion for high crosslinked samples by 2D-Fourier Imaging can explain some of these diffusion features.

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