

## The diffusion of water in poly(ditetrahydrofurfuryl itaconate)

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### Abstract

The diffusion of water into solid poly(ditetrahydrofurfuryl itaconate) (PDTFI) films and in analogous polymer solutions was measured. Diffusion into solid PDTFI films on a glass support was measured in three solutions of different pH (4, 7 and 10) at 37 and 60 °C during a 90 day period. The uptake was high and was both pH and temperature dependent, ranging from 120 to 2000%. A Fickian mechanism is observed for the initial stages of uptake, whilst a non-Fickian mechanism is present when the equilibrium is approached. The pH 7 samples did not equilibrate at any temperature during the experiment. The FTIR investigations of the films indicated some deesterification took place during the uptake. The diffusion coefficients and diffusion exponents are calculated for the samples. The diffusion of water into PDTFI solution in acetone was measured by PGSE-NMR, showing the expected linear attenuation functions. The diffusion coefficient of water was calculated for polymer concentrations up to 10%.

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### 1. Introduction

The methacrylic ester of tetrahydrofurfuryl alcohol has been previously reported to be a promising component of materials for dental and other medical applications [1–3]. Room temperature polymerizing systems based on its polymer were reported to be applicable for tissue repair systems [4], dental applications and drug and fluoride delivery systems [5]. It has biological tolerance by dental pulp, and is superior over other glassy methacrylates in terms of drug delivery.

As a dental material it is used as a comonomer with ethyl methacrylate, hydroxyethyl methacrylate and bisphenol A-glycidyl methacrylate systems [6], in amounts of up to 30% tetrahydrofurfuryl methacrylate (TFMA) by weight, while some investigations of its homopolymer properties have also been reported [7]. Mixtures of varying compositions of an isoprene–styrene copolymer elastomer and

in situ polymerizing tetrahydrofurfuryl methacrylate (SIS/TFMA) form one-gel systems and are used for soft prosthetic applications [8].

The analogous itaconate, poly(ditetrahydrofurfuryl itaconate), PDTFI, has never been investigated in that manner, although polyitaconates are known to be promising materials for dental applications. The advantage of itaconic acid based polymers over methacrylic acid based polymers stems from the fact that itaconic acid can be obtained through fermentation from renewable non-petrochemical sources [9,10] and the lower toxicity of itaconic acid [11].

The diffusion of water into PDTFI was investigated in this paper. In order to obtain more detailed information on the process, diffusion was investigated by following the water uptake of solid polymeric films in contact with water under various pH conditions, and by following by PGSE-NMR [12] the diffusion of water in model polymer solutions. PGSE-NMR has been chosen as it is the only technique that gives a self-diffusion coefficient, and is, at the same time, chemically selective.

Although water uptake was earlier thought to be a surface phenomenon, it is now well-known that this process involves the whole volume of the investigated material, and results of various polymers have been published

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showing that, e.g. poly(methyl methacrylate) and polycarbonates [13] follow a diffusion controlled bulk-absorption process.

## 2. Experimental section

The monomer, ditetrahydrofurfuryl itaconate was prepared by Fischer esterification from itaconic acid and the corresponding alcohol. Monomer was distilled under reduced pressure and polymerized shortly afterwards because of its tendency to polymerize spontaneously. The polymerization was carried out in bulk at 40 °C, using 0.5 mol% 2,2'-azo-bis-isobutyronitrile (AIBN) as the initiator, up to about 20% yield. A more detailed description of the procedure is given elsewhere [14].

For the investigation of diffusion of water in films, the samples were prepared by dissolving the polymer in acetone and evaporating the solvent at room temperature and ambient pressure and subsequently under high vacuum, leaving polymer films on the inner surface of the measuring vehicle. After drying, the samples were immersed into three solutions of different pH and the water uptake was followed at two temperatures, 37 and 60 °C. The water uptake was monitored by measuring the change of sample mass. The samples were measured by taking them out of solution, rubbing by a soft cloth from the outer side of the vehicle and letting water drain from the vehicle for 180 s. After measurement the samples were put back into fresh pH solution.

Film thickness was established by carefully cutting a small part of the film and measuring its thickness. Each sample was subjected to five such measurements at different positions in the vehicle, using an Erichsen Instruments film thickness gauge. The FTIR spectra of dry films were recorded using a Bomem FTIR spectrophotometer.

The early stages of diffusion were followed by the modified approach of Patel and Braden to calculate diffusion in various polymethacrylates [15]. That equation was used for the absorption of a rectangular specimen immersed in water, while the specimen in this investigation was a film and the water penetrated only from one side. So the equation in this case was

$$\frac{M_t}{M_\infty} = \left( \frac{Dt}{l^2} \right)^{1/2} \quad (1)$$

where  $M_t$  is the uptake measured at convenient time intervals,  $M_\infty$  is the equilibrium uptake,  $t$  is time,  $l$  the film thickness and  $D$  the diffusion coefficient that may be calculated from the slope when Eq. (1) is reorganized.

To determine the possible mechanism of the swelling process the diffusion exponent,  $n$ , was calculated using the equation

$$\frac{M_t}{M_\infty} = kt^n \quad (2)$$

This equation may be applied to thin films where diffusion through the edges is insignificant [16] and the value of  $n$  should indicate the dominant mechanism of the water uptake process. The mechanism is Fickian for values of  $n$  equal or less than 0.5. Values of  $n$  between 0.5 and 1 indicate a mechanism where macromolecular relaxations predominate, and values of  $n$  higher than 1 imply that transport relaxation processes control the uptake [17].

The PGSE-NMR measurements were performed on a Bruker AMX 360 ( $^1\text{H}$ ) high resolution NMR spectrometer employing a stimulated echo sequence. Trapezoidal gradient pulses were generated using a Bruker constant current gradient amplifier. Trapezoidal gradient pulses were chosen, as they minimize the gradient pulse strength mismatches that appear as a result of temperature changes in the coils via Joule heating when pulsing large gradients. The self diffusion coefficient was calculated from the Eq. (3) [18].

$$A(G, \delta) = A_0 \exp \left[ -\gamma^2 G^2 \left( \frac{30\Delta(\delta + \sigma)^2 - (10\delta^3 + 30\sigma\delta^2 + 35\sigma^2\delta + 14\sigma^3)}{30} \right) D_s \right] \quad (3)$$

where  $A(G, \delta)$  is the measured peak integral in the presence of gradient pulses of intensity  $G$ , duration  $\delta$  and ramp time  $\sigma$  over a diffusion timescale of  $\Delta$ . All experiments were performed at 25 °C.

## 3. Results

### 3.1. Diffusion of water into solid polymer

The time dependence of the water uptake of the films is shown in the following figures.

The results given in these two figures show significant variations of the water uptake at different pH, as well as at different temperatures.

The equilibrium uptake in the specified period was attained only in the cases of pH 4 and 7 at the lower temperature, together with possible but not fully confirmed equilibrium at pH 4 at 60 °C (Figs. 1 and 2). All the other samples did not reach equilibrium within the experimental time, 90 days. It is also interesting to note that the order of the amount of the water uptake was not the same at both temperatures. Analysis of the experimental results at both temperatures shows that the least amount of water was absorbed at pH 4 and 37 °C. After 90 days there was a much larger uptake at pH 10 than at pH 7, while the 60 °C the degree of uptake was reversed. A comparison of the amount of water at different temperatures at the end of the experimental period showed that the value was about 2.5

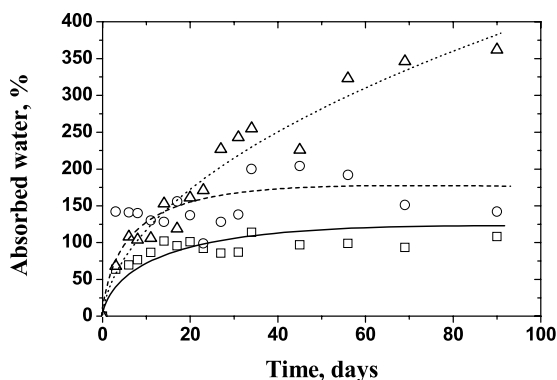


Fig. 1. The time dependence of water absorption of PDTFI films at pH 4, squares, pH 7, circles, and pH 10, triangles, at 37 °C.

times higher at pH 4 and 10, while the value was about 12 times greater at pH 7.

All the samples were insoluble in acetone and other solvents after the experiment was terminated, indicating the probable occurrence of crosslinking.

The FTIR spectra of these polymers did not differ from the spectra of the untreated sample, except in the appearance of a peak around  $1576\text{ cm}^{-1}$  that was non-existent in the spectrum of the untreated polymer. This peak is also missing in the spectra of both pH 4 samples, and the sample swollen at pH 7 and 37 °C. These differences are shown in Fig. 3.

The spectra also reveal the increased amount of water in the samples that could not be removed after excessive drying under vacuum at room temperature (the mass of all the samples after drying was about 2% greater than the mass before the start of the experiment and the samples could not be dried to reach the original mass).

Having calculated the equilibrium water uptake, the absorption plots  $M_{\infty}/M_t$  vs.  $t^{1/2}$  are shown in Fig. 4.

All samples showed linear behaviour at pH 4 and 10, while the samples at pH 7 showed non-linear behaviour at 37 °C, while in case of the same pH at 60 °C equilibrium was not attained, so the data for the plots could not be calculated.

A logarithmic representation of these data was used to

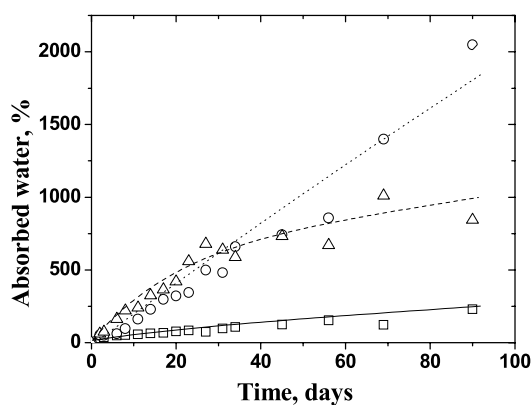


Fig. 2. The time dependence of water absorption of PDTFI films at pH 4, squares, pH 7, circles, and pH 10, triangles, at 60 °C.

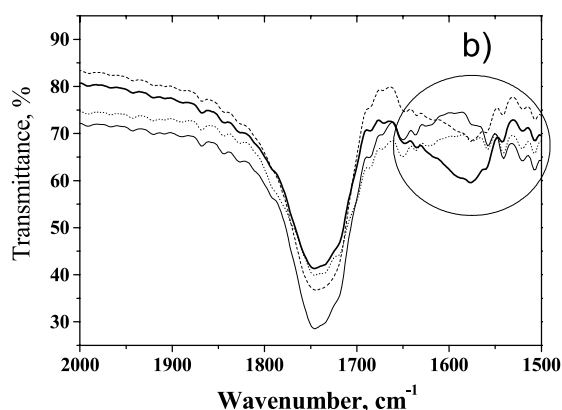
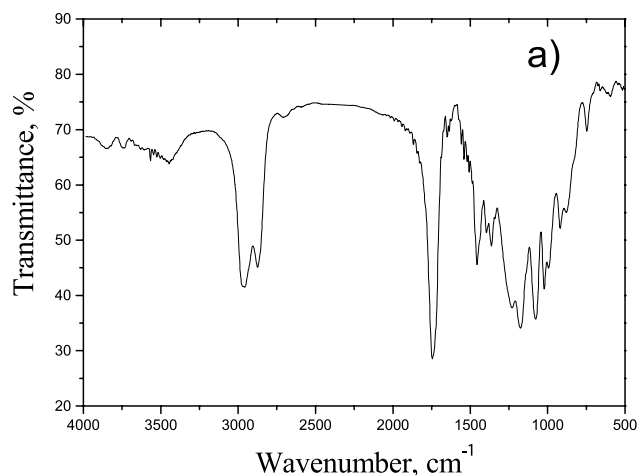


Fig. 3. (a) The FTIR spectrum of untreated PDTFI. (b) The difference at  $1576\text{ cm}^{-1}$  of different samples of PDTFI, the upper bold line is the untreated sample, the lower bold line is the pH 10, 60 °C sample, the dotted line is pH 4, 60 °C and the dashed line is pH 10, 37 °C.

determine the diffusion exponent, and these are presented in Fig. 5.

According to the results of the experiments at 37 °C, the driving force responsible for the swelling at pH=4 and pH=10 is simply the diffusion of the solvent into the polymer, which results in a Fickian swelling behavior. At 60 °C the same trend was observed for pH=4, while the results at pH 10 indicate that the diffusion mechanism changes from Fickian to non-Fickian.

The diffusion coefficients and diffusion exponents obtained from these data are presented in Table 1, together with the percentage of water absorbed at equilibrium. The

Table 1

The diffusion coefficients of the equilibrated samples, the values of the diffusion exponent and the percentage of water absorbed at the equilibrium

Temperature (°C)	pH	$D \times 10^{-11}$ (m <sup>2</sup> /s)	$n$	Equilibrium (%)
37	4	1.67	0.28	120
37	10	5.01	0.50	360
60	4	3.32	0.41	230
60	10	20.1	0.92	990

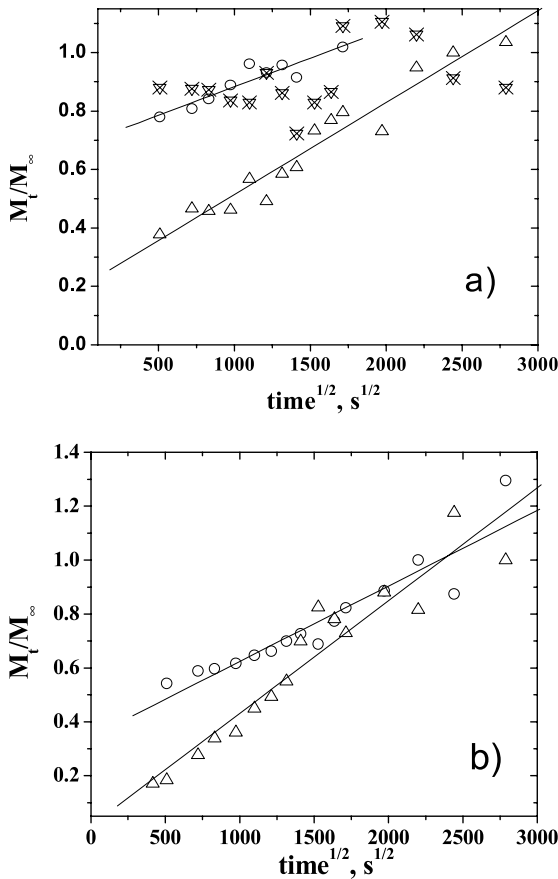


Fig. 4. The absorption plots for PDTFI at 37 °C (a) and 60 °C (b), the pH 4 samples are given as circles, the pH 7 as crossed down triangles, and pH 10 as up triangles.

samples swollen at pH 7 were omitted from the table due to their specific behaviour.

The diffusion coefficients of these samples were calculated for every experimental point and are shown in Fig. 6.

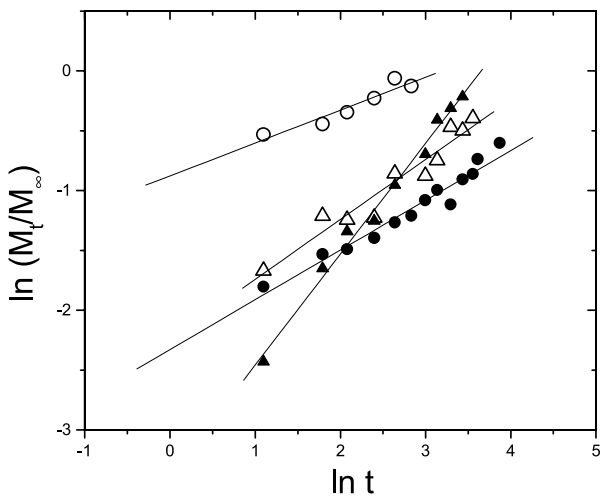


Fig. 5. The logarithmic absorption plots of the water uptake, used for determination of the diffusion exponent,  $n$ . The pH 4 samples are given as circles, and pH 10 as up triangles. The open points are 37 °C, while the solid ones are 60 °C.

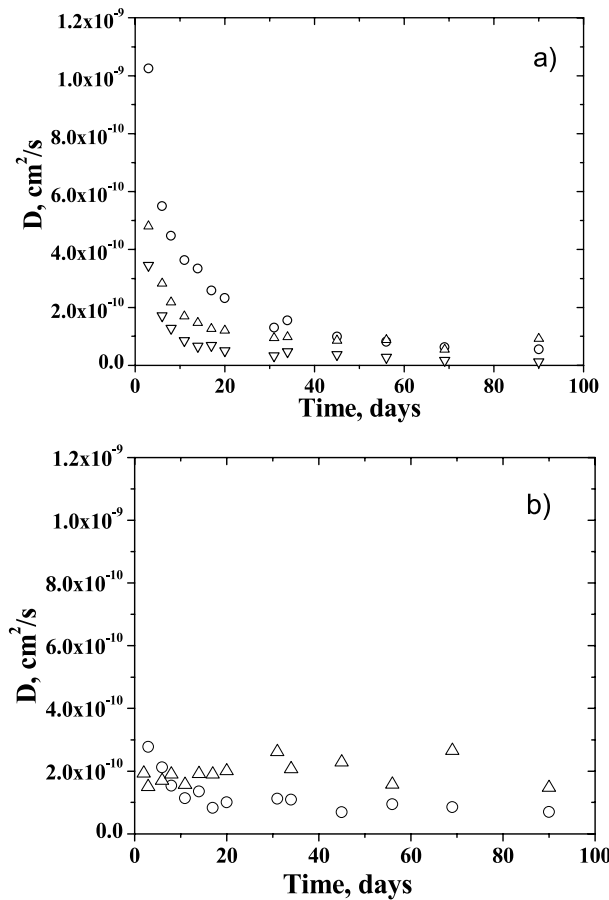


Fig. 6. The diffusion coefficients at 37 °C (a) and 60 °C (b), the pH 4 samples are given as circles, the pH 7 as down triangles, and pH 10 as up triangles.

The diffusion coefficients decreased with time and tended to equilibrate after about 20 days in the case of the samples subjected to swelling at 37 °C. At the higher temperature equilibration took place relatively rapidly, except for the samples at pH 7, where no equilibration could be observed, thus the diffusion coefficients could not be determined for these samples. The average values of the diffusion coefficients in the equilibrated region are given in Table 2.

### 3.2. The diffusion of water within model polymer solutions investigated by PGSE-NMR

The diffusion of water in the polymer solutions in acetone is shown in the following figures. The attenuation plots in Fig. 7 are linear over two orders of magnitude of

Table 2  
Diffusion coefficients for PDTFI in the equilibrated region

Temperature (°C)	pH	$D \times 10^{-11}$ (m <sup>2</sup> /s)
37	4	7.44
37	10	9.45
60	4	8.85
60	10	20.8

signal intensity. The diffusion coefficients obtained from the fits of the first region are given in Fig. 8.

#### 4. Discussion

This water absorbing system was prepared from an uncrosslinked polymer, polymerized to a low yield, in order to ensure the dominant presence of linear chains. Consequently, the degree of absorption was expected to be larger than in similar previously investigated systems.

All the samples became opalescent soon after immersion in water. It seems that the adsorption is similar to the previously reported adsorption of PTHM, where water forms clusters, probably by reorganization of the tetrahydrofurfuryl rings. This behaviour was already mentioned in a previous paper where the dipole moments of TFM were calculated [7]. The dipoles on the THFI monomer calculated in the same manner shown in Fig. 9 confirm the possibility of such reorganization.

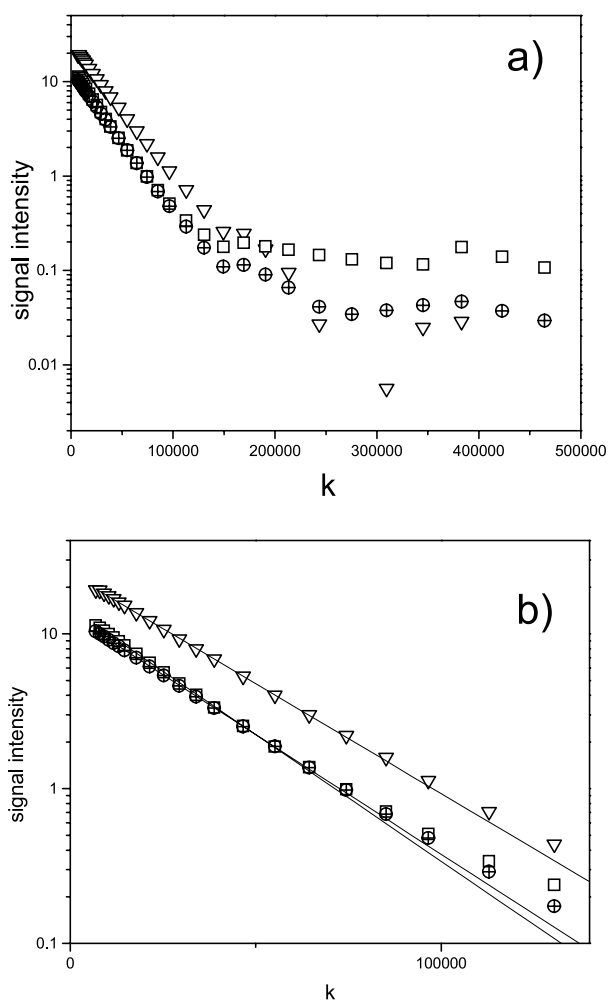


Fig. 7. Attenuation function for water, ( $\square$ ) 1% solution PDTFI, ( $\oplus$ ) 5% and ( $\nabla$ ) 10% solution of PDTFI (a) the whole range, (b) the region of faster diffusion.

There are two such rings in each monomer unit, so there is a relatively high possibility that the rings will adjust in the most appropriate manner to form clusters. This can explain the existence of two mechanisms of water absorption in the samples that reached equilibrium: (a) An initial one, where saturation of the polymer matrix is the dominant process, and (b) cluster forming, when saturation of the matrix has been attained. Such behaviour is similar to the previously reported behaviour of PTFM [7], and PTFM-poly(ethyl methacrylate) copolymer [19]. The initial period in PDTFI samples at 37 °C lasts about 10 days, while at 60 °C the period is, as expected, much shorter.

The interesting fact in these samples was that the absorption differed with changing pH. This is characteristic of systems in which dissociation occurs. PDTFI has no groups that can easily dissociate under the conditions applied, and the possibility of the tetrahydrofurfuryl ring opening is highly unlikely, for such reactions occur under much harsher experimental conditions [20]. In order to explain this behaviour, it was necessary to find a way to investigate whether dissociation could take place.

There is a striking difference in behaviour in some samples that did not fully attain equilibrium and where, in some cases, the mass of absorbed water exceeded 1000%. These samples were the pH 10 sample at 37 °C and the pH 10 and 7 samples at 60 °C. The FTIR spectra of these samples revealed some differences compared to the spectrum of the untreated sample. The spectra of the samples that reached equilibrium showed no significant differences from the untreated sample spectrum.

The new peak that developed at 1576  $\text{cm}^{-1}$  is most probably the peak of the carboxylic group that can form by hydrolysis of the ester group. These samples also have a more intensive broad peak in the 3400  $\text{cm}^{-1}$  region. This phenomenon is normally attributed to water, which can be the effect of the water that remained in the sample and was not removed by simple room temperature high vacuum drying. The intensity of the peak was not very strong, showing that the hydrolysis did not take place to a large extent, but that the process was probably continuous, increasing the amount of hydrolyzed groups with time. It is suspect that there are no significant changes in mass of such samples after drying. The hydrolysis should reduce the polymer mass, but this effect is probably masked by the higher amount of water that remained in the sample. Such behaviour is interesting because similar investigations of PTFM showed that no hydrolysis occurred [7], although the pH dependence of the water uptake was not studied for that system. No hydrolysis was observed only in the PDTFI samples at pH 4 and 7 at the lower temperature investigated, which were also the only samples where equilibrium was attained. At this moment there is insufficient evidence to link the impossibility to reach equilibrium of the other samples solely to hydrolysis.

Investigation of the absorption plots shows that only the pH 7 samples show non-linear behaviour. Such behaviour in



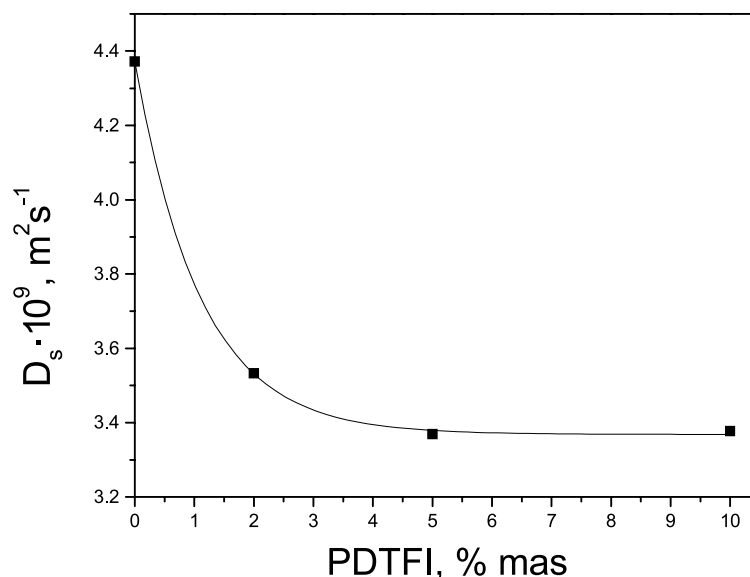


Fig. 8. The self diffusion coefficients of water in deuterated acetone solution of PDTFI, where  $k = \gamma^2 G^2 [30\Delta(\delta + \sigma)^2 - (10\delta^3 + 30\sigma\delta^2 + 35\sigma^2\delta + 14\sigma^3)]/30$ .

previous investigations has been linked to the extraction of water-soluble materials [2]. This is consistent with the assumption that some hydrolysis takes place, although it is still unclear why there is no non-linearity in the pH 10 samples. This absence may be linked with the fact that itaconic acid is fully dissociated in aqueous solutions and present as a dianion only at pH values larger than eight. That could mean that the carboxylic groups present as a result of dissociation are mostly probably dissociated at pH 10. At pH 7 possibly some dissociation occurs, but not complete, so the system is very sensitive to minor variations, giving the huge dissipation of experimental results between the measurement points. It is interesting to call attention to the earlier investigation of poly(ethyl methacrylate)/tetrahydrofurfuryl methacrylate [2] that was carried out at neutral pH, where the system showed significant variations of the results for different samples.

The diffusion coefficients calculated for each experimental point show that they consistently decrease in the first part of the process, which is expected, taking into account that

significant accumulation of water takes place in the samples in that period. This is the unsteady state diffusion, and the concentration is changing with time. Because of that the diffusion coefficients, which are concentration depend, decrease. Once the system is diluted enough the values of the coefficients tend to stabilize. As expected, that process is much faster at 60 than at 37 °C.

The PGSE-NMR investigations of water diffusion within model polymer solution have shown that with increasing polymer concentration, the diffusion coefficient of the water decreases. There may be two origins for this—a simple obstruction effect in which the solvent has to diffuse around the polymer segments thus lengthening its diffusion path length or an increase in the binding of the solvent molecules to the polymer. When the shape of curve in Fig. 8 is compared to the previous investigations by Davies and Griffiths on the effects of obstruction and binding for the diffusion of small molecules in polymer solutions [18], it can be seen that the departure from the straight line in the given concentration range was present only in samples where the retarding force experienced by the probe molecules was not only due to obstruction, but to specific interactions between the probe molecule and the polymer. It may mean that in this system similar specific interactions are also present. Still, the huge difference in the diffusion coefficients between polymer in solution and in solid state, as given in Table 1 show that the obstruction effects play the major role in controlling the diffusion of water in PDTFI.

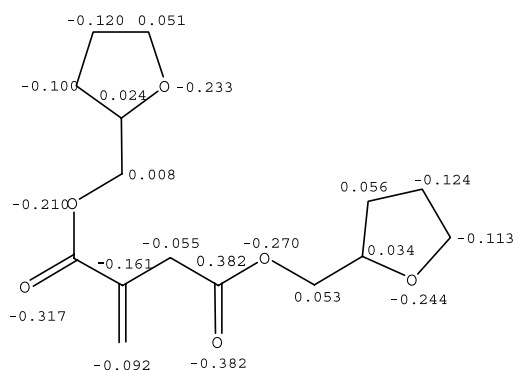


Fig. 9. Dipoles on the DTFI monomer unit calculated using PM3 (convergence limit 0.01) for energy minimization and MM+force field for molecular dynamics at 300 K.

## 5. Conclusion

This investigation has shown that the water uptake behaviour of PDTFI is similar to that of corresponding methacrylic systems. PDTFI is a promising material for

applications where methacrylates, especially PTFM, are currently used. The results also show that the pH range where the polymer is used is of critical importance for its applications and duration of use. As itaconic acid derivatives are usually less toxic than analogous methacrylates, easier to handle, and the acid is produced from non-petrochemical sources, this study confirms the potential interest of poly(itaconates) as an alternative to poly(methacrylates).

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