Water sorption in polymer network films synthesised from PEO oligomers containing acrylic and vinyl ether functionalities

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Summary
Poly(ethylene oxide) oligomers, with end groups that have either acrylic or vinyl ether functionalities, were photopolymerised by UV radiation to create polymer networks in the form of thin films. Moisture sorption of the polymers, determined by microgravimetric analysis, was correlated to the oligomer structure, i.e. to the PEO chain length and to the type of unsaturation. The data can be described with a Fickian diffusion model using diffusion coefficients of water in the polymer networks on the order of 1×10^{-12} m^2/s. The total amount of water sorption at equilibrium saturation increases with an increasing number of EO units in the oligomer used to synthesise the network.
The number of absorbed water molecules associated with each EO unit increases with the number of these units in the oligomer until it reaches two water molecules per EO unit, for acrylated-PEO oligomers (PEGDA) having at least 30 EO units. The type of interactions between the polymer network and water were evaluated by means of thermal analysis performed on the hydrated films. It was found that all water is present as bound rather than mobile water.

Introduction
The investigation on the interactions of water with hydrophilic polymers is gaining importance both for theoretical reasons and for biological and environmental applications, such as in biopolymers and antifouling coatings. Water uptake in hydrophilic polymer films and coatings has been investigated by many techniques, ranging from gravimetry (1) to swelling measurements (using neutron reflectivity (1) and ellipsometry (2)) as well as techniques that characterise absorbed water, such as solid state nuclear magnetic resonance (NMR) (3,4) and differential scanning calorimetry (DSC) (3,5). NMR and DSC analyses gave evidences of different types of water present in the hydrated systems, from the most tightly-bound to the free, bulk-like water (6,7).
Among the many hydrophilic systems described in the literature, an extensive research was devoted worldwide to the study of the hydrophilic properties of PEO-based polymers. The papers published include the investigation on the interaction both with liquid water (8,9) and with water vapour (10). Whereas in PEO homopolymers the presence of crystallinity decreases the humidity uptake (11), a very high hydrophilicity can be obtained in copolymers which contain EO units. Consequently, it has been proposed that the latter are suitable for humidity sensors (10).

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Previously we reported the preparation of polymer films from PEO oligomers. The oligomers, having different molecular weight were functionalised with different unsaturations in the α-ω positions, namely acrylic (12) or vinyl-ether double bonds (13). They were subjected to curing by means of the photopolymerization technique. This technique assures an easy preparation of the films based on the PEO oligomers and leads to the formation of networks having full insolubility in water, as the conversion of the double bonds is complete. The thermal and dynamic-mechanical properties of the films were also investigated and correlated to the oligomer molecular structure, in particular to the kind of functional end group present in the molecule and to the oligomer MW (12,13). The films obtained showed a high humidity sorption clearly due to the presence of the PEO chains and their properties could be modulated changing the molecular weight of the PEO chain.

Pursuing the characterisation of these systems, in this work we compare the hydrophilic properties of the networks obtained from the acrylic or vinyl ether double bonds and investigate the factors which allow to tailor the hydrophilicity of the photocured networks. Oligomer MW and type of functionality are the main parameters taken into account.

Experimental

Acrylated-PEO oligomers (PEGDA) were prepared as reported previously (12). Vinyl ether PEO oligomers (DVE) were kindly supplied by BASF and used as received. Table 1 lists the MW, the end group concentration and the EO content of the PEGDA and DVE oligomers used in this study. $\overline{M}_n$ measurements were carried out through VPO (Gonotec Osmomat 070) at 37°C in $CHCl_3$. Acrylic functionality was determined by the saponification method (12).

Table 1: Properties of the oligomers used

Oligomer	$\overline{M}_n$ [a]	Functional end groups (mol^{-1})	EO Content N[b]	% w/w[c]
TEGDA	252	2.0	2.9	52.4
PEGDA 400	514	2.0	8.8	77.0
PEGDA 600	733	1.8	13.8	84.0
PEGDA 1000	821	1.7	15.8	85.7
PEGDA 1500	1579	1.8	33.1	92.0
DVE2	158	2.0	2.0	55.7
DVE3	202	2.0	3.0	65.3
DVE4	268	2.0	4.5	73.8

(a) Determined by VPO. Error range: ± 2%
(b) number of EO units per molecule of oligomer
(c) weight % of EO units in the oligomer

The PEGDA and DVE oligomers were cured by radical and cationic polymerisation mechanisms, respectively. The curing procedure is described elsewhere in detail (12,13). The conversion of the double bonds was checked by means of FTIR analysis by evaluating the signal of either the acrylic or the vinyl ether unsaturation at about 1620 cm^{-1}. In all cases, the conversion was found to be nearly complete (>96%).

$$\delta = 21.66 \text{ MPa}^{(1/2)}$$

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        |
        O
        |

—CH₂-CH—
        |              δ=20.14 MPa^(1/2)
    O=CO—
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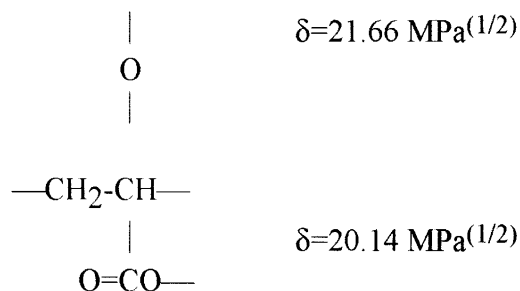
The value of δ for the poly(vinyl ether) chain is higher than that of the poly(acrylate) chain; therefore a greater hydrophilicity of the poly(vinyl ether) compared to the poly(acrylate) system can be foreseen.

Table 2: Moisture sorption for PEGDA films

Oligomer	Moisture sorption (w/w %) after 15 hrs	H_2O molecules/EO units
TEGDA	4.1	0.3
PEGDA 400	24.0	0.8
PEGDA 600	44.0	1.4
PEGDA 1000	55.1	1.6
PEGDA 1500	81.0	2.2
DVE 2	39.2	1.5
DVE 3	37.0	1.4
DVE 4	43.3	1.6

In order to compare the kinetics of water uptake of different films, the mass change at a given time, M(t), such as recorded in Figure 1, was divided by the equilibrium mass uptake obtained at long time, M(∞). In all cases, the normalised mass uptake was found to increase nonlinearly with the time of exposure to water, t, as expected for Fickian diffusion. This result is in agreement with the work of other authors [15], which determined that the water transport in PEO crosslinked at high temperature in the presence of 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3 can be described with Fickian dynamics.

Our data can be fitted to a simple model describing Fickian diffusion into a planar sheet [16]. The normalised water mass uptake is given by the equation:

$$\frac{M(t)}{M(\infty)} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(\frac{-(2n+1)^2 \pi^2}{4h^2} Dt \right), \tag{1}$$

where h is the film thickness and D is the diffusion coefficient of water in the polymer network. Figure 2 shows a typical plot of experimental data and the best fit to equation 1, using only D as a variable in fitting.

Films with a final thickness of about 200 µm were cast onto glass substrates. Cured films were peeled off the substrate and stored in a desiccator in an anhydrous atmosphere. The moisture sorption measurements were performed using a Cahn microbalance (DCA 322), evaluating the weight increase of the film as a function of time, maintaining it at 25°C in air (R.H.= 100%). DSC measurements were performed on a Mettler DSC 30 instrument at 10°C/min in the range −100/+120°C.

Results and discussion

Figure 1 shows the water mass uptake for six polymer films as a function of time. The curves show that the humidity sorption of all the films increases with time with an asymptotic trend. After about 15 hours the water sorption saturates at a plateau value If one compares these maximum values of the water uptake, it is clear that they increase with increasing the MW of the oligomer, i.e. the number of EO units present in the molecule used to create the network. The effect of the MW of the oligomer on the humidity sorption of the cured films at saturation is reported in Table 2.
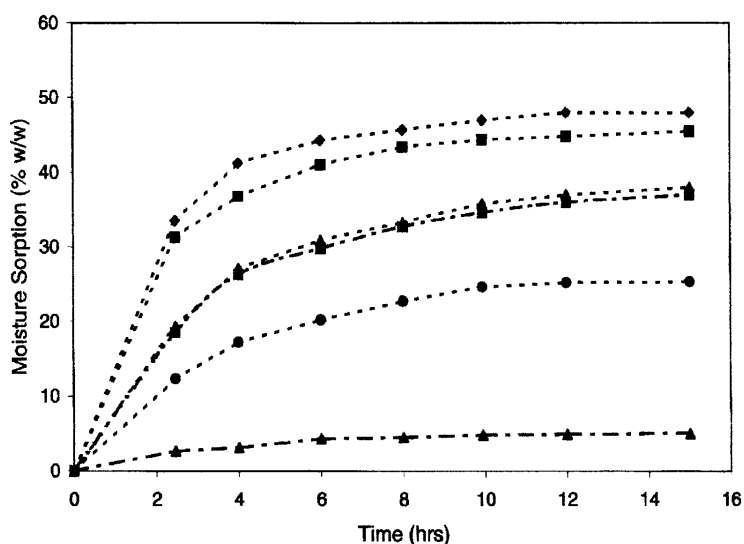

Figure 1: Moisture sorption of six cured films as a function of the time of exposure to humidity-saturated air. The solid lines are a guide to the eye. The data are shown by the following symbols: (---▲---) TEGDA; (···●···) PEGDA400, (---■---) DVE2, (···▲···) DVE3, (···■···) PEGDA600, (···◆···) DVE4

By comparing the curves of Figure 1 concerning the acrylic and the vinyl ether oligomers with a similar number of EO units (e.g. TEGDA and DVE3), it is apparent that the latter ones are clearly more hydrophilic than the former ones. The PEGDA oligomers have a high humidity sorption only in the presence of long PEO chains, while the hydrophilic DVE oligomers absorb moisture even with short PEO chains. This finding can be interpreted on the basis of the higher solubility parameter value (δ) of the vinyl ether structure compared to that of the acrylate. By using the group contribution method (14), taking into account the dispersion and the polar and the H-bond contributions, the following values are obtained.
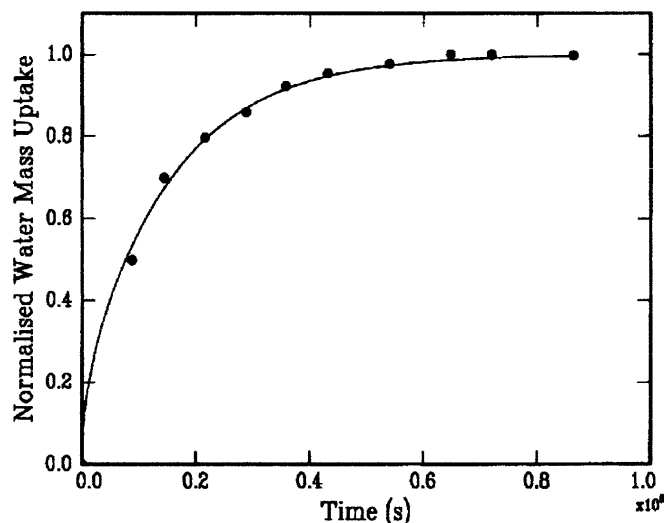
$$-CH_2\text{-}CH-$$
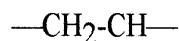
Figure 2: Normalized water mass sorption as a function of the time of exposure (DVE 3 film: the solid line shows a plot of Eq. 1 using the best fit value of D, 1.02×10^{-12} m^2/s)

A good fit to Equation 1 was obtained in all cases using three terms in the series. The best-fit values of D for the PEO networks were all in the range between 1.0 and 1.8 x 10^{-12} m^2/s, without a clear dependence of D on the PEO chain length. In high MW PEO crosslinked by a peroxide, a value of 26 x 10^{-12} m^2/s was calculated by other workers (15). This significantly higher value of D can be attributed to the higher PEO MW and to a lower crosslinking density of the network.

We next consider in more detail how the chain length is related to the total water uptake. In Table 2 the number of absorbed water molecules associated with *each* EO unit is reported. For the PEGDA oligomers, a maximum value of about two water molecules per EO unit is obtained for the oligomer having about 30 EO units. In a previous paper (8), by investigating PEO-water interactions in solution, the formation of stable complexes containing three moles of water per ether group was evidenced. The discrepancy with the present results could be attributed to the different experimental conditions (vapour phase instead of liquid phase), the equilibrium water uptake strongly depends on.

In the case of the DVE oligomers, the data reported concern only short PEO chains. In the range of chain length examined here, the number of water molecules per EO unit is nearly constant and is about 1.5.

Finally, we consider the state of the absorbed water. As reported in previous works (3-5), hydrated polymers contain different types of water mainly distinguished as bound water (which is non-freezable) and freely-diffusable water (which is freezable). These two types of water can be distinguished by means of DSC analysis. The thermograms obtained for the hydrated films do not show any endothermic peak, associated with the melting of ice crystals. This result indicates that there is no freely-diffusing water within the hydrated films. In Figure 3 a typical DSC trace of a PEGDA 600 film before and after moisture sorption is reported: the decrease of the T_g value after moisture sorption is clearly evident.
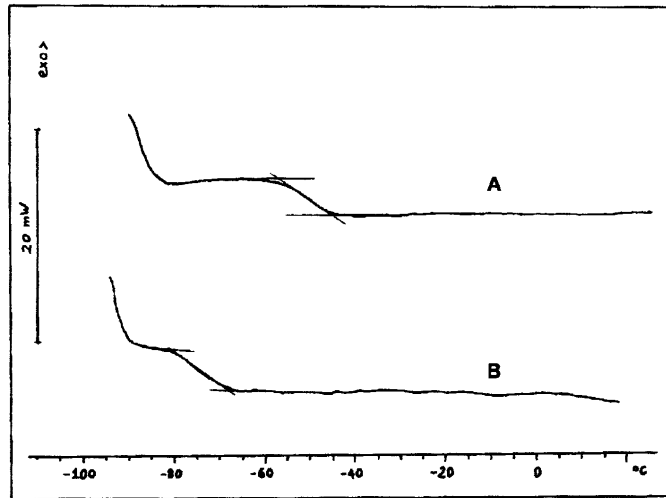
Figure 3: DSC thermograms of a PEGDA 600 film before (A) and after (B) moisture absorption (moisture uptake = 44.0 w/w %)

Table 3 collects the measured values of the T_g for polymer films of the PEGDA series, obtained before and after moisture sorption.

Table 3: Glass transition temperatures of PEGDA films before and after moisture sorption

Oligomer	T_g (K)		
	Before moisture absorption	After moisture absorption	
		Experimental	Calculated*
TEGDA	293	263	271
PEGDA 400	236	211	207
PEGDA 600	221	199	190
PEGDA 1000	211	191	183
PEGDA 1500	211	198	173

*Using Equation 2 and measured values of equilibrium water uptake.

A consistent decrease in T_g after water exposure is evident, which indicates a water plasticisation effect as reported by other investigators (6,17). The T_g of concentrated polymer solutions can be predicted from known values of solvent volume fraction (ϕ_s) using an equation proposed by Kelly and Bueche (18):

$$T_g = \frac{Tg_{pol} + (KTg_{solv} - Tg_{pol})\phi_s}{1 + (K-1)\phi_s},$$

(2)

where Tg_{pol} and Tg_{solv} represent the glass transition temperatures of the polymer and solvent, respectively, and K is a constant related to the thermal expansivities of the glass and melts of the two substances. Taking for the T_g of water a value of 170 K (as estimated previously by NMR measurements (3)) and assuming the value of K to be 2.5, which is a

typical value, we can calculate the values of T_g expected using the measured values of water sorption. Table 3 compares these calculated values with the experimental ones and reveals good agreement. The values are within 10 K for all oligomers except for PEGDA 1500. This discrepancy can be interpreted by considering that in this case the network is heterogeneous. Besides the Tg, the DSC thermogram shows a fusion peak at +18°C, due to the crystallinity of the PEO chain. The crystallinity disappears after the water uptake, indicating that the water molecules interact also with the crystalline segments of the network.

Conclusions

The interaction of water with different types of polymeric networks containing PEO segments was considered. The hydrophilic properties increase as a function of the length of the PEO chain. By comparing diacrylated oligomers with the DVE homologues, a higher hydrophilicity of the latter ones is shown, in agreement with the higher value of the solubility parameter. The number of water molecules bound to each EO unit was found to reach a maximum value of about two for the PEGDA oligomers having a sequence of at least 30 EO units. The uptake of water by the networks was described with Fickian dynamics and a diffusion coefficient of the order of 1×10^{-12} m^2/s, which is lower than the value obtained in the literature for a more open network. The DSC analyses showed that all the water is bound to the polymeric network determining a decrease of the Tg of the network, clearly related to the humidity uptake.

Acknowledgements

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