

Physical ageing and modelling of the glass-liquid transition of water and aqueous solutions imbibed in poly-(2-hydroxyethyl-methacrylate) and in the bulk state

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Physical ageing of glassy water and aqueous solutions of 22 mol% ethylene glycol and 16 mol% lithium chloride imbibed in poly(2-hydroxyethyl-methacrylate) (PHEMA) and of the bulk solutions was studied by differential scanning calorimetry (DSC). The samples were isothermally annealed for a constant time at various temperatures below their glass \rightarrow liquid transition temperature. The resulting DSC scans were analyzed in terms of the four-parameter model of Moynihan et al., which incorporates both the non-exponentiality of the relaxation function and the structure dependence of the retardation times. The non-exponentiality parameter, β , is smaller for the solutions imbibed in PHEMA than in the bulk, implying a broader distribution of retardation times and/or enhanced cooperativity of the relaxation process. The activation enthalpy and the parameter x , describing the structure dependence of relaxation, are on average the same whether the solutions are imbibed in PHEMA or in their bulk states. However, x varies systematically with thermal history, indicating that the phenomenology is not completely accurate. It is probable that the treatment of non-linearity by the model needs to be improved.

1. Introduction

Hydrophilic polymers imbibe large amounts of water and aqueous solutions without dissolving in them. These so-called hydrogels have a number of important medical applications, e.g., for soft contact lenses or as depot media for controlled release of drugs [1,2]. These polymers, being porous on a molecular level, provide a matrix in which the imbibed liquid can act as a medium for the transport of selected ionic and non-ionic species, ranging in size from oxygen (O_2) to globular proteins [3].

When the liquid is imbibed in the polymer, both its structure and its dynamics become modified [4,5], first by the surface energy of the polymer matrix and second by H-bonded interactions

with the hydrophilic groups of the polymer chain. In our previous studies [6,7], differential scanning calorimetry (DSC) showed that water imbibed in a hydrophilic polymer, namely poly(2-hydroxyethyl-methacrylate) or PHEMA, can be vitrified by quenching in liquid nitrogen and that it undergoes a glass \rightarrow liquid transition at 162 ± 2 K for a heating rate of 30 K min^{-1} , which seems to be associated with the 'freezable' amount of water because it disappeared upon its crystallization. We had also found that the temperature of the glass transition, T_g , as well as the width and the shape of the DSC scans in the glass transition region, of bulk solutions of ethylene glycol (EG) and LiCl in water were modified when they were imbibed in the PHEMA hydrogel.

Here we present the results of a study investi-

gating the effect of physical ageing on the calorimetric properties of the glass \rightarrow liquid transition of water and aqueous EG and LiCl solutions imbibed in PHEMA. Physical ageing, i.e., annealing of a glass below T_g , results in changes in many physical properties such as complex relative permittivity, complex mechanical modulus, density, enthalpy, etc., of which the latter can be conveniently studied by DSC methods. The decrease in enthalpy during annealing is recovered during heating to a temperature above T_g and this recovery usually leads to a maximum in the heat capacity, C_p , in the glass transition range. The particular shape of the DSC scan in that region depends sensibly both on the relaxation kinetics of the material under study and on the thermal history employed. Since both EG and LiCl solutions can be vitrified in their bulk states by quenching in liquid nitrogen, changes in their relaxation behavior in going from the bulk to the hydrogel can be directly studied by comparing their behavior on physical ageing in both states. This comparison can be parameterized using the phenomenological Tool-Narayanaswamy (TN) model [8-10] of the glass \rightarrow liquid transition kinetics described by Moynihan *et al.* [11] and further developed by Hodge and co-workers [12,13].

This model is characterized by two essential features: non-exponentiality and non-linearity. It linearizes the kinetics by using the method of Gardon and Narayanaswamy [9,10], considers heating and cooling as a series of small temperature steps, and applies Boltzmann superposition of non-exponential responses. The response function is chosen to be of the Kohlrausch-Williams-Watts [14,15] form:

$$\phi(t) = \exp\left[-(t/\tau_0)^\beta\right], \quad (1)$$

where $1 \geq \beta \geq 0$ and $\phi(t)$ is normalized so that $\lim_{t \rightarrow 0} \phi(t) = 1$ and $\lim_{t \rightarrow \infty} \phi(t) = 0$. τ_0 is a retardation time which depends on temperature, T , and fictive temperature [8], T_f , as

$$\tau_0 = A \exp\left(\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right), \quad (2)$$

where A , x ($1 \geq x \geq 0$) and Δh^* are parameters and R is the ideal gas constant. The four param-

eters β , A , x , and Δh^* are assumed to be independent of T and T_f . Hodge and Berens [12] introduced annealing into the cooling cycle, and Hodge and Huvard [13] used an optimization technique based on the Marquardt search routine in order to obtain best fit parameters. The thermal history (cooling rate, heating rate, annealing temperature and annealing time) and Δh^* were input and the best fit values of A , x , and β were output. Implementation of the model on a computer and the optimization procedure for obtaining the best fit parameters are given in detail elsewhere [12,13].

2. Experimental

Pure PHEMA samples were obtained from Smith and Nephew, London, and were purified and characterized by the manufacturer. The PHEMA used for all the studies absorbs a maximum amount of 34% water (by weight) on complete swelling at ambient temperature. For solutions the maximum amount of uptake depended on the solute; it was 49 wt% for EG and 53 wt% for LiCl.

Weighed amounts of as-received PHEMA were kept in water, 22 mol% EG-H₂O solution and 16 mol% LiCl-H₂O solution for about 1 week. The surface of the PHEMA hydrogel samples was quickly dried with tissue paper to remove excess bulk liquid, and then weighed again to determine the amount of water or solution in the hydrogel. EG obtained from Fluka and LiCl from Ventron were both used without further purification.

A Perkin-Elmer differential scanning calorimeter, model DSC-4, with the TADS computer-assisted data acquisition was used for all studies. Curvature of the DSC traces was eliminated by the SAZ function, which subtracts during scanning a baseline obtained with empty sample pans. Samples were dried quickly before being crimp-sealed into Al pans. The weight of the samples ranged between 10.9 and 23.0 mg.

In order to compare the experimental data, $C_p(\text{exp})$, with the output from the model, $C_p(\text{cal})$, the former were normalized with respect to the difference between liquid and glassy heat capaci-

ties, C_{pl} and C_{pg} , respectively:

$$C_p^N = \frac{C_p(T) - C_{pg}(T)}{C_{pl}(T) - C_{pg}(T)} \quad (3)$$

The temperature dependences of C_{pl} and C_{pg} were obtained by linear extrapolation of the liquid- and glassy-state data.

Two similar sets of thermal histories were used. For the first set, which was not parameterized by the TN model, the sample was sealed in an Al pan, quenched by immersing in liquid nitrogen, transferred to the precooled DSC instrument, heated to the annealing temperature at 30 K min^{-1} , annealed for 90 min, cooled to 103 K at 30 K min^{-1} , and scanned at 30 K min^{-1} . The second set of histories was parameterized, and was identical to the first except that cooling and heating was performed at 10 K min^{-1} . This history differed slightly from that used for the parameterization calculations [12,13,19]. For the latter, a quench rate of 1000 K min^{-1} estimated by Plattner and Bachmann [20] was assumed, and annealing was introduced during cooling from above T_g to the starting temperature for scanning, without any additional heating or cooling to or from the annealing temperature. The differences between actual and assumed thermal histories are small, and it is unlikely (but possible) that they contributed to the relatively poor fits to some of the histories.

3. Results

The results for the first set of thermal histories described above are shown in figs. 1–3. Figure 1 shows the DSC scans of pure water in PHEMA following annealing for 90 min at 130, 136, 143, and 147 K (curves 1–4, respectively). The annealing temperatures are marked with an arrow.

Figure 2(a) shows the DSC scans of a 22 mol% EG/H₂O solution in the bulk phase following annealing at 125, 129, and 134 K. Figure 2(b) shows the DSC scans of the same solution imbibed in PHEMA after annealing at 131, 135, and 143 K (curves 1–3 in both figures; annealing temperatures are marked by arrows). Figure 3(a)

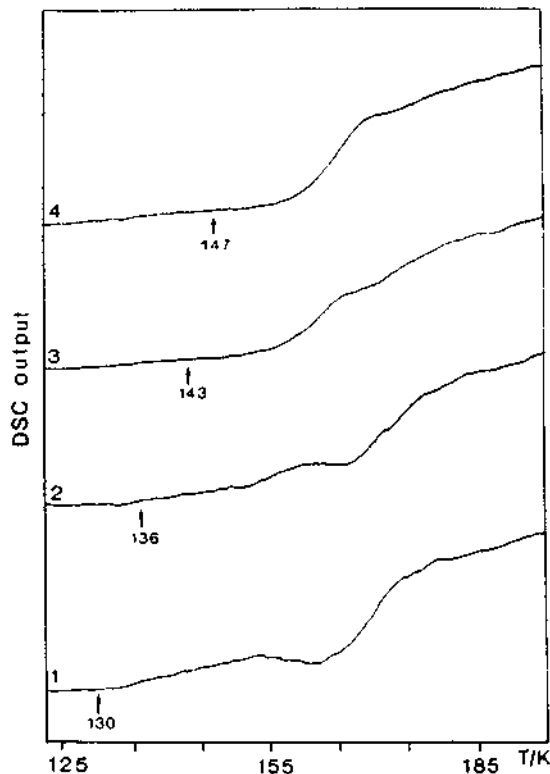


Fig. 1. Influence of the annealing temperature on the glass \rightarrow liquid transition of pure water in PHEMA, as observed in the DSC scans at a heating rate of 30 K min^{-1} . Curves 1–4 are for annealing at 130, 136, 143, and 147 K, in each case for 90 min. The weight of the samples used was 20.5 mg (1, 2) and 23.0 mg (3, 4) (both containing 34 wt% of water). The curves are drawn on the same scale with respect to the imbibed water. The annealing temperatures are given in K and are marked by arrows. The temperature axis is not corrected for the thermal lag of the instrument. See text for thermal history details.

shows the DSC scans of a 16 mol% LiCl/H₂O solution in the bulk phase after annealing at 118, 128, 133, and 136 K, and fig. 3(b) shows data for the same solution imbibed in PHEMA after annealing at 138, 143, 147, and 153 K (curves 1–4 in both figures). The annealing temperatures of the bulk samples were chosen such that the difference between T_{ann} and T_g was about the same in the bulk and the hydrogel. All curves in figs. 2 and 3 are drawn on the same scale with respect to the weight of EG/H₂O and LiCl/H₂O solution, respectively.

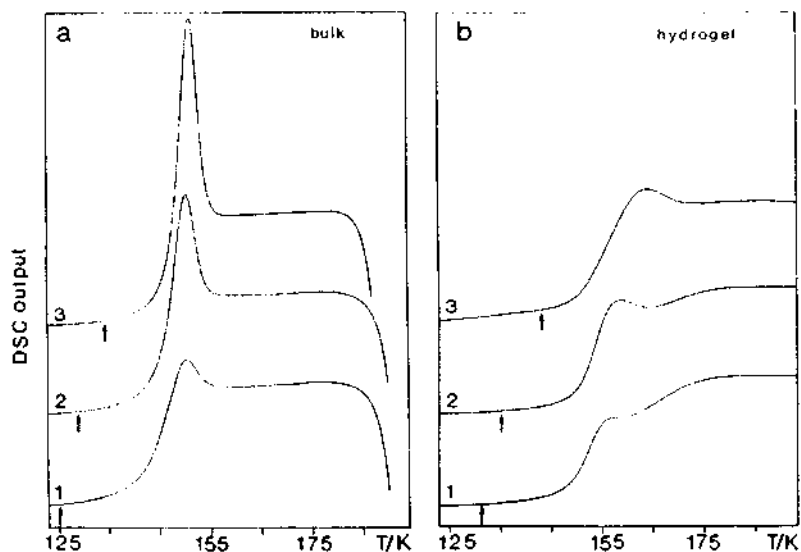


Fig. 2. Influence of annealing temperature on the glass \rightarrow liquid transition of 22 mol% EG/H₂O solution in the bulk and in PHEMA hydrogel, as seen in the DSC scans. (a) Curves 1–3 are for annealing the bulk solution at 125, 129, and 134 K. The weight of the sample used was 21.6 mg. (b) Curves 1–3 are for annealing the hydrogel at 131, 135 and 143 K. The weight of the sample (containing 49 wt% solution) used was 19.7 mg. The annealing time was 90 min in all cases. The curves are normalized with respect to the weight of EG/H₂O solution. The annealing temperatures are given in K and are marked by arrows. The temperature axis is not corrected for the thermal lag of the instrument. See text for thermal history details.

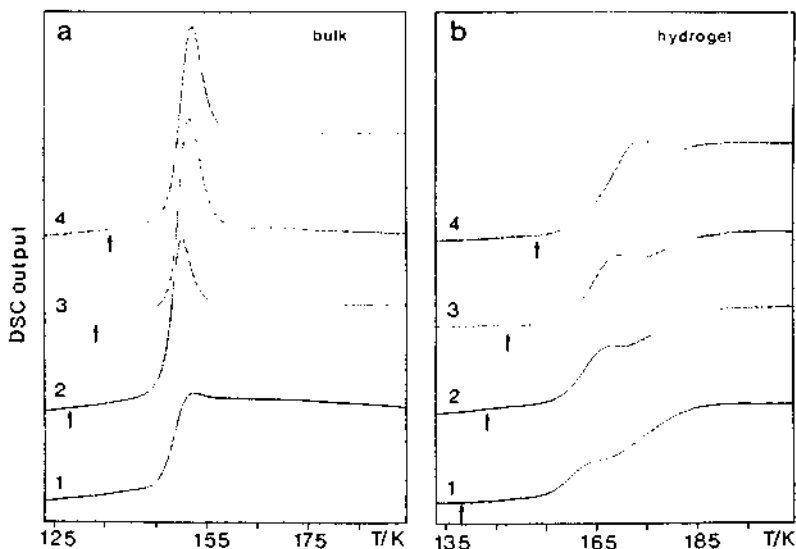


Fig. 3. Influence of annealing temperature on the glass \rightarrow liquid transition of 16 mol% LiCl/H₂O solution in the bulk and in PHEMA hydrogel, as seen in the DSC scans. (a) Curves 1–4 are for annealing the bulk solution at 118, 128 and 133, and 136 K. The weight of the sample used was 14.9 mg. (b) Curves 1–4 are for annealing the hydrogel at 138, 143, 147, and 153 K. The weight of the samples (containing 55 wt% solution) used was 10.9 mg (1, 2, 4) and 11.6 mg (3). The annealing time was 90 min in all cases. The curves are normalized with respect to the weight of LiCl/H₂O solution. The annealing temperatures are given in K and are marked by arrows. See text for thermal history details.

The scans of the bulk samples show a peak at the upper end of the glass \rightarrow liquid transition, that becomes higher with increasing annealing temperature. This behavior is well known for a great variety of low- and high-molecular-weight glasses [11], and was first quantified by Petrie [16] for polystyrene. All scans of the hydrogels show a sub- T_g endothermic peak at the low temperature end of the glass \rightarrow liquid transition region. This peak shifts to higher temperatures and becomes better resolved for higher annealing temperatures. Such behavior is known for glassy polymers

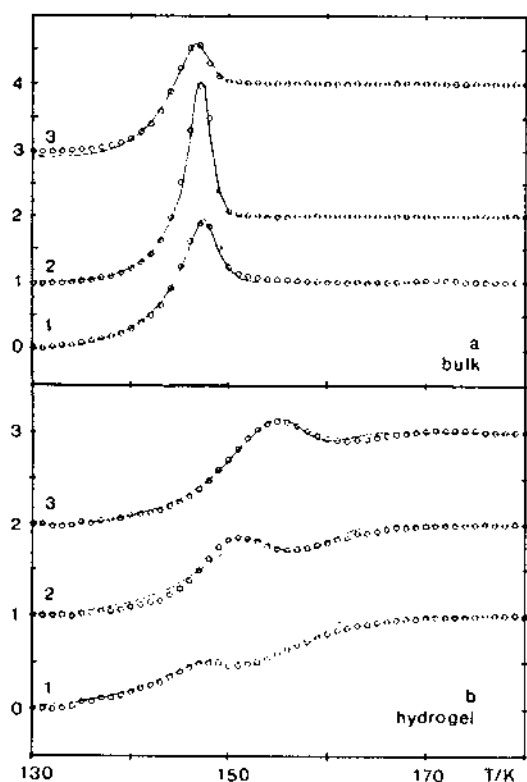


Fig. 4. Calculated and experimentally obtained DSC traces in the glass \rightarrow liquid transition region of 22 mol% EG/H₂O solutions in the bulk and in the PHEMA hydrogel. Experimental data are normalized according to eq. (3) and are shown as open circles; best-fit curves using the parameters given in table 1 are shown as full lines. (a) Curves 1–3 are for annealing the bulk solutions at 130, 135, and 141 K for 90 min. (b) Curves 1–3 are for annealing the solutions in the hydrogel at the same temperatures for the same time. The cooling and heating rates used for parameterization were 1000 and 10 K min⁻¹, respectively.

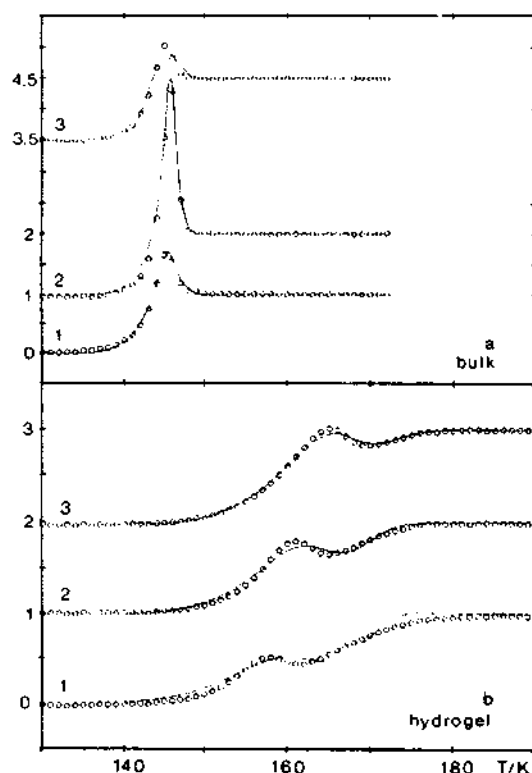


Fig. 5. Calculated and experimentally obtained DSC traces in the glass \rightarrow liquid transition region of 16 mol% LiCl/H₂O solutions in the bulk and in the PHEMA hydrogel. Experimental data are normalized according to eq. (3) and are shown as open circles; best-fit curves using the parameters given in table 2 are shown as full lines. (a) Curves 1–3 are for annealing at 127, 136, and 141 K. (b) Curves 1–3 are for annealing the solutions in the hydrogel at 142, 147, and 153 K. The annealing time was 90 min in all cases. The cooling and heating rates used for parameterization were 1000 and 10 K min⁻¹, respectively.

such as poly(vinylchloride) [17,18] and poly(methylmethacrylate) [19], but it has not been observed before in low-molecular-weight glasses.

Figures 4 and 5 show a comparison of experimentally obtained normalized DSC scans (open circles) with calculated C_p^N values obtained from the TN formalism (full lines) for the EG and the LiCl solutions, respectively. No attempt at fitting the data for the pure H₂O hydrogel was made because ΔC_p at T_g is much smaller in this case and the calorimetric signal contained more noise.

Table 1

Best-fit parameters for modelling the glass \rightarrow liquid transition for a 22 mol% EG/H₂O solution in PHEMA and in the bulk for annealing at different temperatures T_{ann} . The annealing time was 90 min, Δh^* was held constant at 100 kJ mol⁻¹. χ^2 is defined as $(\sum_i^N (C_p(\text{exp})_i - C_p(\text{cal})_i)^2)$

Sample	T_{ann} (K)	x	β	$-\ln A$ (s)	χ^2
EG/H ₂ O	130	0.42	0.43	75.29	0.11
PHEMA	135	0.45	0.40	75.28	0.10
	141	0.52	0.35	75.79	0.03
average	-	0.46	0.39	75.45	-
EG/H ₂ O	130	0.43	0.57	80.92	0.04
bulk	135	0.56	0.70	81.66	0.13
	141	0.48	0.66	81.92	0.08
average	-	0.49	0.64	81.50	-

An unambiguous determination of C_{pg} and C_{pl} was also difficult due to curvature of the scans.

Figure 4(a) shows data for a 22 mol% EG/H₂O solution in the bulk phase after annealing at 130, 135, and 141 K. Figure 4(b) shows data for the same solution imbibed in PHEMA after annealing at the same temperatures (curves 1–3 in both figures). Data for the 16 mol% LiCl/H₂O solution in the bulk phase after annealing at 127, 136, and 141 K are shown in fig. 5(a). Figure 5(b) shows data for the same solution imbibed in PHEMA after annealing at 142, 147, and 153 K.

A set of best fit parameters $\ln(A)$, x , β and Δh^* was obtained for each of the thermal histo-

ries shown in fig. 4 and 5. These parameters are summarized in table 1 for the 22 mol% EG/H₂O solutions and in table 2 for the 16 mol% LiCl/H₂O solutions. We obtained the best fits with an activation enthalpy, Δh^* , of 100 kJ mol⁻¹ which is in reasonable agreement with the value of 80 ± 20 kJ mol⁻¹ found in our previous study [7] by the method of Moynihan et al. [21], using the heating rate dependence of T_g . We also varied the cooling rate for one particular thermal history for a 22 mol% EG/H₂O solution and found that a cooling rate of 125 K min⁻¹ gave a slightly better best-fit residual, but this cooling rate is an order of magnitude smaller than that found experimentally by Plattner and Bachmann [20] for the cooling of similar-sized specimens. Nevertheless, it may well be that some of the scatter in the parameters for the different thermal histories is attributable to uncertainties in the cooling rate. For both the EG and LiCl solutions, β is higher in the bulk state than in the hydrogel phase. For EG/H₂O, the difference is smaller (β_{average} : bulk: 0.64 ± 0.1 , hydrogel: 0.39 ± 0.1) than for LiCl/H₂O (β_{average} : bulk: 0.93 ± 0.1 , hydrogel: 0.39 ± 0.1). The difference in the x parameter for the bulk and hydrogel states is small both for EG/H₂O (x_{average} : bulk: 0.49 ± 0.1 , hydrogel: 0.46 ± 0.1) and for LiCl/H₂O (x_{average} : bulk: 0.68 ± 0.1 , hydrogel: 0.67 ± 0.1). For the hydrogel samples, there seems to be a systematic variation of the x and β parameters with annealing temperature, x becoming larger with higher annealing temperatures and β becoming slightly smaller with higher annealing temperature.

Table 2

Best-fit parameters for modelling the glass \rightarrow liquid transition for a 16 mol% LiCl/H₂O solution in PHEMA and in the bulk for annealing at different temperatures T_{ann} . The annealing time was 90 min, Δh^* was held constant at 100 kJ mol⁻¹. χ^2 is defined as $(\sum_i^N (C_p(\text{exp})_i - C_p(\text{cal})_i)^2)$

Sample	T_{ann} (K)	x	β	$-\ln A$ (s)	χ^2
LiCl/H ₂ O	142	0.54	0.44	70.15	0.16
PHEMA	147	0.66	0.40	70.82	0.05
	153	0.81	0.33	70.62	0.04
average	-	0.67	0.39	70.53	-
LiCl/H ₂ O	127	0.63	0.90	82.02	0.02
bulk	136	0.62	1.04	82.13	0.14
	141	0.79	0.84	82.15	0.12
average	-	0.68	0.93	82.10	-

4. Discussion

In fig. 1, the DSC scans of pure water imbibed in PHEMA show very broad sub- T_g maxima in C_p that shift to higher temperatures with increasing annealing temperature and eventually merge with the C_p step of the glass \rightarrow liquid transition. Figures 2(b) and 3(b) show the same behavior for the EG- and LiCl solution hydrogels whereas the bulk solutions of EG and LiCl show an overshoot in C_p at the upper edge of the glass \rightarrow liquid

transition region that becomes higher when the annealing temperature is increased. This, together with the broadening of the glass transition range for the hydrogel samples, indicates substantially altered relaxation behavior for a liquid at its T_g when it is imbibed in a hydrophilic polymeric matrix.

The results of our modelling study demonstrate that the reason for the different relaxation behavior is a decrease in the value of β in going from the bulk to the hydrogel, whereas x is on average similar both in bulk and in the hydrogel (both at constant Δh^*). Since β is associated with the width of the distribution of retardation times [9] or with degree of cooperativity of the relaxation process, originating either from hierarchically constrained motions of atomic groups of various size [22,23] or from coupling of a primary relaxing species to surrounding groups [24], this means that in the hydrogel the spectrum of retardation times is considerably broadened and/or the cooperativity of molecular rearrangements is enhanced in comparison with the bulk state of the solutions. A hydrogel is thought to be composed of a system of interconnected pores, 15–30 Å in diameter [3], which are continuously fluctuating and redistributing in size due to the thermal motion of the polymer chains. Enhanced cooperativity of molecular motions of the low molecular weight constituents of the hydrogel could simply be caused by the geometrical constraints of the confinement of those molecules in small pores. On the other hand, an actual distribution of retardation times may result as a consequence of a distribution of molecular environments in which the molecules relax.

Apart from the observation that the value of β is lower in the hydrogel than in the bulk solutions of EG and LiCl, we further note that β is identical for both solutions imbibed in PHEMA, whereas it is considerably different for the bulk solutions. This strongly suggests that the distribution of enthalpy retardation times for the solutions imbibed in PHEMA is controlled mainly by the polymeric matrix.

Broad distributions of retardation times, or more general non-exponential decay functions such as eq. (1), result in the relaxation of a glass

becoming dependent on its previous thermal history. This dependence is the basis for the well known 'cross-over' or 'memory' effects [25–28] where, after annealing for a certain period of time at a temperature, T_1 , and then increasing the temperature abruptly to T_2 , one observes that the enthalpy [28] (or any other relaxing quantity, such as volume [25,26] or shear modulus [27]) recorded as a function of time first increases, reaches a maximum value, and finally monotonically decreases towards the value of metastable equilibrium. The observed sub- T_g peaks in the DSC scans of the hydrogels are a direct analogue to such 'memory' behavior in a temperature scan instead of an isothermal experiment (apart from the fact that not H itself but a quantity proportional to $\partial H/\partial T$ is recorded).

The mean value of the β parameter for the bulk LiCl solution is 0.93 ± 0.1 , thus reaching its limiting value of 1.0 within our experimental uncertainty. This means that the relaxation is purely exponential in this case, or stated differently that there is only a single ordering parameter governing the enthalpy relaxation process in this material at T_g . This type of behavior is highly unusual, since most materials studied so far using the TN formalism ranging from polymer systems to molecular glasses have values of β between 0.25 and 0.70 [19].

Finally, we discuss the relatively large scatter in the values of the optimum parameters for the same sample when subjected to different thermal histories. As already mentioned, this scatter may be partly due to uncertainties in the cooling rate, but in order to obtain slightly better fits to the data one must reduce the cooling rate by an order of magnitude, which is certainly outside the possible experimental scatter of cooling rates which result from quenching the encapsulated sample in liquid nitrogen. Therefore, we believe that the scatter in the optimum parameters cannot be entirely attributed to experimental uncertainties. Studies of Tribone et al. [29] on various kinds of poly(methylmethacrylates) showed a similar systematic variation of the x parameter with thermal history, whereas differences in β were small. They concluded that this difference may be due to an incorrect handling of the non-linearity

of the relaxation kinetics by the TN model [8-10], and our data tend to confirm this. The small temperature variation of the β parameter is in contrast to the assumption of the TN model that β is independent of temperature. It is not clear whether this temperature variation of β could be removed by using an improved expression for the structure dependence of the relaxation process or a different relaxation function. We only want to mention that there are other models, e.g., the coupling scheme of Ngai et al. [24], where the β parameter is an explicit function of temperature.

5. Conclusions

We have studied physical ageing of glassy water and aqueous EG and LiCl solutions imbibed in PHEMA and, in the case of the aqueous solutions, also in the bulk state. The DSC scans have been analyzed in terms of the four-parameter TN model of the glass transition kinetics developed by Moynihan et al. [11] and Hodge et al. [12,13]. The retardation time spectrum of the solutions becomes broader when they are imbibed in the PHEMA matrix. The enthalpy relaxation in bulk 16 mol% aqueous LiCl solution can be described by one single retardation time. Systematic changes in the values for the parameter describing the structure dependence (and hence the non-linearity) of the relaxation process with thermal history have been found. These suggest a deficiency in the TN model.

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