Effect of initial sample anisotropy on the solvent sorption kinetics of glassy poly(2-hydroxyethyl methacrylate)

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When moving solvent fronts meet at the centre of a glassy polymer during sorption of solvent, making the sample entirely rubbery, sudden changes in the area, thickness and sorption rate typically occur. Examination of the sorption of water and methanol by glassy poly(2-hydroxyethyl methacrylate) showed that the magnitudes and directions of these changes can be readily modified by creating anisotropic stresses within the glassy polymer by controlled deformation of the sample prior to solvent sorption. However, the transport mechanism and sorption kinetics were not significantly altered by differing levels of initial sample anisotropy.

(Keywords: poly(2-hydroxyethyl methacrylate); anomalous transport; diffusion; sorption; swelling kinetics)

INTRODUCTION

The complex solvent sorption kinetics of glassy polymers has attracted substantial theoretical and experimental interest over the decades due to its implications for understanding solvent transport and relaxation processes in polymers. Work in this area has also been driven by the desire to use glassy polymers as the rate controlling agent in delivery systems for bioactive compounds[1]. In monolithic delivery systems, the drug is initially dispersed or dissolved in the glassy polymer and the solute release rate is controlled by the polymer swelling rate and the velocity of the moving solvent front[2–4]. Another type of device uses swelling polymer gels as pistons to pump the solute from a reservoir through an orifice[5–7]. The sorption kinetics of superabsorbent polymers, which are typically glassy when dry, are also of considerable technological interest.

A glassy, initially isotropic polymer sample which becomes rubbery during solvent sorption undergoes complex dimensional changes (except for spherical samples), as illustrated in *Figure 1* for slab geometry. Shortly after exposure to the solvent, sharp penetration fronts develop which advance towards the centre of the sample. These penetration fronts are typically assumed to be the point of the glass-to-rubber transition, although this might not always be true[8]. Several research groups have noted that as long as a glassy core of polymer is present, the outer, solvent-swollen rubbery layer swells only in the direction of diffusion, as the glassy core resists stresses tending to cause isotropic expansion of the sample[8–11]. Thus, the increase in the sample's volume due to solvent sorption appears as an increase in thickness while the area remains virtually constant, as illustrated in *Figure 1*. This constrained swelling causes the development of compressive stresses in the direction of diffusion and tensile stresses perpendicular to the direction of diffusion, also shown in *Figure 1*. However, once the moving fronts separating the unswollen glassy core and the outer rubbery sheath meet towards the centre of the sample, the constraint imposed by the glassy core is relieved. At this point, the sample undergoes rapid dimensional rearrangement in response to the anisotropic stresses. These stresses cause the area of the now rubbery sample to increase at the expense of the thickness, until an isotropic state is reached. This rearrangement is typically so rapid that it occurs at nearly constant volume, and leads to a sudden increase in the instantaneous sorption rate because of the decrease in the diffusional path length and the increase in diffusional area. Swelling past this point occurs virtually isotropically until equilibrium is reached[11]. In contrast to this complex behaviour, when an initially rubbery polymer sample absorbs solvent and swells, it simply expands isotropically until the equilibrium volume is reached, as illustrated in *Figure 2*.

In piston-type delivery devices, unidirectional expansion of the gel is desired since expansion in area may rupture the reservoir. In monolithic devices, the sudden decrease in thickness and expansion in area could lead to a sudden increase in the solute release rate, which may or may not be desirable. Furthermore, the rapidity of the dimensional rearrangements implies that substantial stresses develop within the glassy core during the initial stages of swelling. Stresses in the glass have been postulated by several authors to significantly affect the sorption kinetics[12–15]. Thus, it is worthwhile to gain a better understanding of the dimensional changes, the effects that they have on the sorption kinetics and transport mechanism, and the extent to which they can be eliminated or enhanced by altering the stress profiles within the glass.

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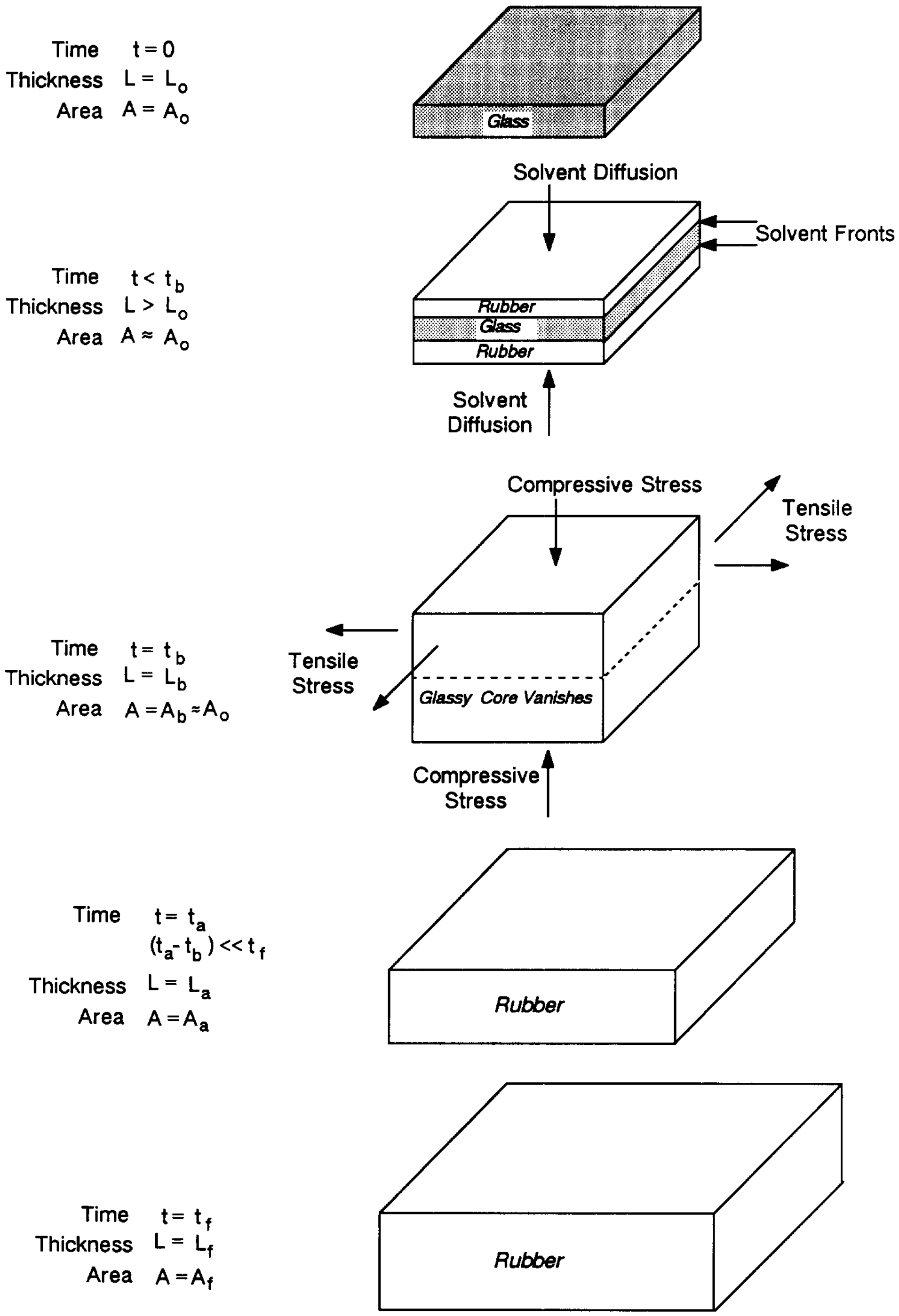

Figure 1 Dimensional changes and related phenomena observed upon swelling a glassy polymer sheet in a good solvent

THEORY

Properties of glassy polymers are known to be history-dependent, in part because of the capability of glassy polymers to sustain significant levels of internal stress. Since the dimensional rearrangements caused by solvent sorption are caused by the stresses within the glassy polymer, we believed that the dimensional changes could be modified by altering stresses within the glassy gel prior to solvent sorption. In previous work, we showed that this could be done by swelling a polymer sheet in a solvent, then drying it with a fixed area in a gel dryer. (This device is manufactured to dry gel electrophoresis gel slabs at constant area in order to preserve the bands of separated proteins or DNA molecules. It works by applying a tensile stress via suction over the surface area while drying the sheet, thus resisting the contraction that normally accompanies drying[11].) A polymer sample dried to a glassy state in this fashion could maintain stresses that were tensile in the direction of diffusion (i.e. thickness) and compressive perpendicular to diffusion (i.e. area), as illustrated in *Figure 2*. Since swelling tends to cause expansion in area and thickness, these stresses are largely relieved by swelling.

Table 1 Categorization of sorption phenomena based upon the dimensional changes that accompany the disappearance of the glassy core

Type	Thickness	L_a/L_b	Area	A_0/A_a	Rate of sorption
1	Decrease	<1	Increase	<1	Increase
2	Constant	1	Constant	1	Constant
3	Increase	>1	Decrease	>1	Decrease

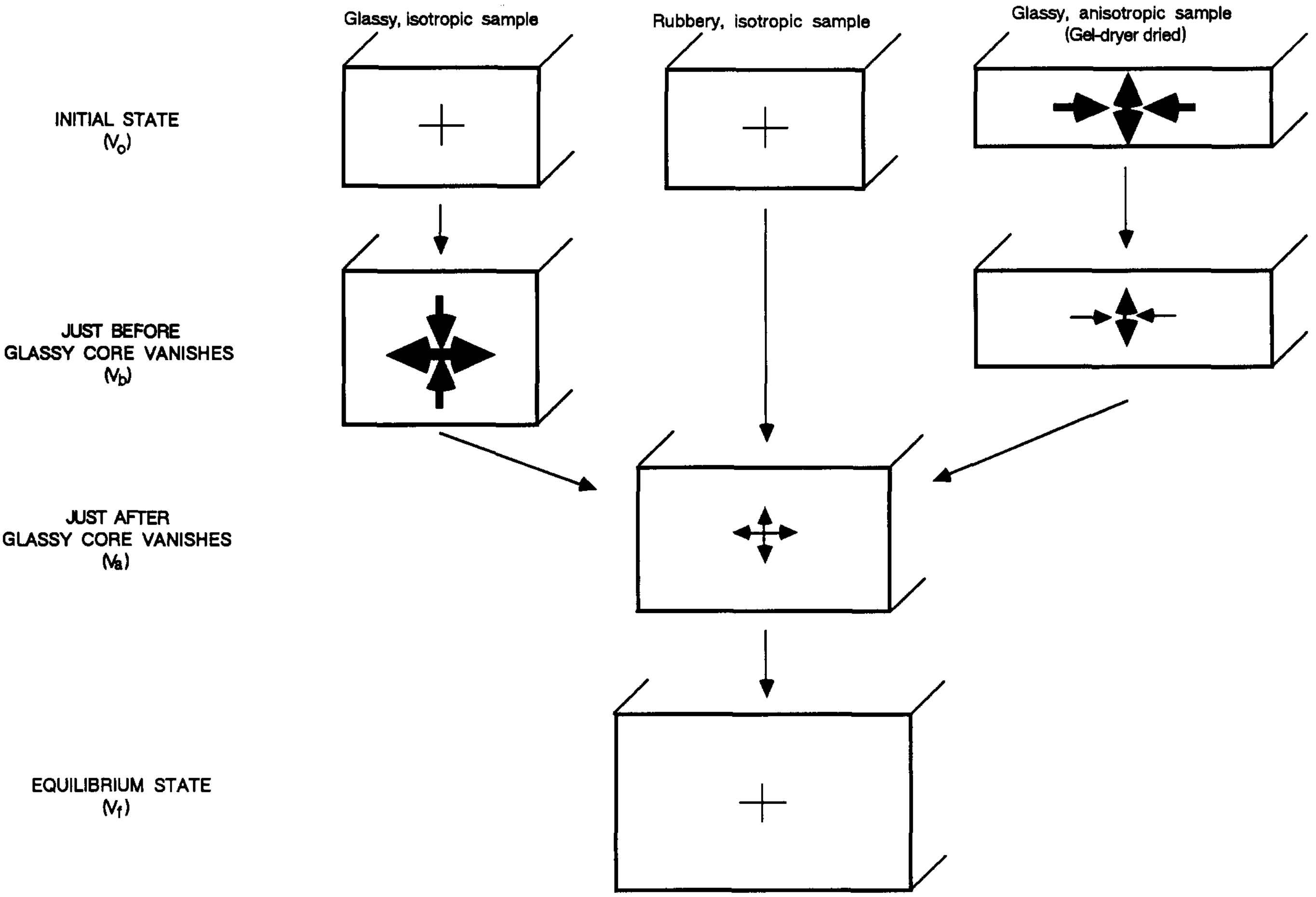

Figure 2 Side view schematic of dimensional changes of polymer sheets during sorption, categorized by initial state of the polymer. Arrowheads indicate the direction of stress, while their weight qualitatively indicates the magnitude of the stress

This contrasts with initially isotropic samples, where the constrained, one-dimensional swelling causes anisotropic stress to build up (*Figures 1* and *2*). As a result, for a gel dryer dried sample, relatively small changes of dimensions in directions opposite to initially isotropic samples occur as the result of the disappearance of the glassy core, as illustrated schematically in *Figure 2*. Thus it was apparent that variations in preparation technique could cause diverse types of dimensional changes.

Regardless of the preparation technique, all glassy polymer samples can be categorized as one of three types according to the direction of change in the sample dimensions which occur immediately after the moving solvent fronts meet at the centre of the sample eliminating the glassy core, making the sample entirely rubbery. This often occurs at about 50% of the equilibrium solvent uptake, although this is widely variable[16]. The three types of dimensional changes which could occur upon disappearance of the glassy core are: an increase in area and a decrease in thickness, resulting in an increase in the instantaneous sorption rate; no change in any dimension; or a decrease in area and an increase in thickness, causing a decrease in the instantaneous sorption rate. For convenience, these cases have been designated types 1, 2 and 3, respectively, and their characteristics are summarized in *Table 1* and illustrated in *Figure 3*. Conventionally prepared, initially stress-free samples fall into the category of type 1, which also includes samples which have been compressed in area and expanded in thickness relative to the stress-free glassy state, or which have been stretched in area less than type 2 samples. A type 2 sample is a special case, prepared such that the initial glassy area is greater and the initial thickness less than isotropic stress-free glassy samples; these samples contain anisotropic stresses which are tensile in the direction of thickness and compressive perpendicular to this. In a type 2 sample, the initially anisotropic stresses are almost exactly relieved by the anisotropic swelling which occurs prior to the disappearance of the glassy core; since there are essentially no anisotropic stresses left at this point, dimensional changes do not occur as the result of the core's disappearance. This special state can be achieved by preparing a sample such that the initial area A_0 of the glass polymer is deformed to equal A_a, the area just after the glassy core vanishes and the resulting dimensional rearrangements are complete. Type 3 samples are prepared with deformations and stresses in the same directions as type 2 samples, but at a greater level, so that a contraction in area and an increase in thickness occurs when the glassy core disappears.

The changes in thickness, L, which occur when the glassy core vanishes are directly related to the changes in area, A, since the dimensional rearrangements occur quickly relative to the total sorption time and thus at nearly constant volume. By definition, the sample volume just before the glassy core vanishes is $V_b = L_bA_b$ and the sample volume just after the glassy core vanishes is $V_a = L_aA_a$. Since $V_b \approx V_a$ and $A_0 \approx A_b$, $L_a/L_b = A_0/A_a$. In other words, the ratio of the thicknesses after and before

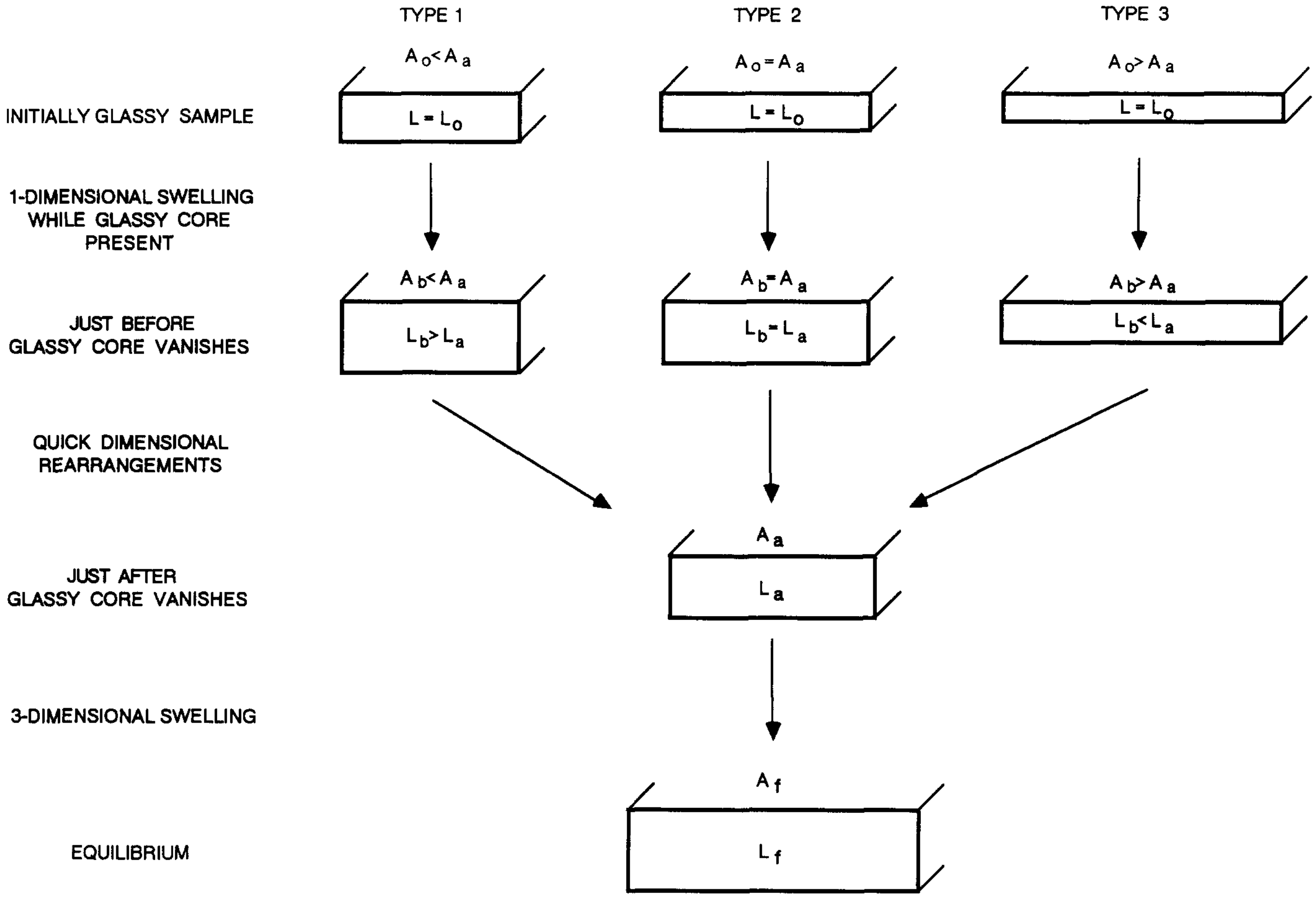

Figure 3 Side view schematic of dimensional changes of polymer sheets during sorption, categorized by the dimensional changes which occur upon disappearance of the glassy core

Table 2 Sorption data from *Figure 4*. Water transport in glassy PHEMA is diffusion controlled and independent of sample thickness

Initial thickness (mm)	Transport exponent n	Diffusion coefficient (D (10^7 cm^2 s^{-1}))	Swelling ratio q	A_0/A_a	L_a/L_b
0.60 ± 0.03	0.50 ± 0.01[a]	1.1 ± 0.1	1.63 ± 0.01	1.12 ± 0.02	1.05 ± 0.03
0.78 ± 0.02	0.51 ± 0.01	1.2 ± 0.1	1.63 ± 0.01	1.14 ± 0.01	1.05 ± 0.02
1.14 ± 0.01	0.51 ± 0.01	1.2 ± 0.1	1.63 ± 0.01	1.13 ± 0.02	1.03 ± 0.03
1.25 ± 0.02	0.50 ± 0.01	1.2 ± 0.1	1.63 ± 0.01	1.12 ± 0.02	1.03 ± 0.03
1.35 ± 0.03	0.51 ± 0.01	1.1 ± 0.1	1.62 ± 0.01	1.12 ± 0.02	1.05 ± 0.01

[a] 95% confidence intervals

the disappearance of the glassy core is inversely proportional to the area ratio. These changes in dimensions are illustrated schematically in *Figure 3* for sample types 1, 2 and 3. Since rubbery samples do not maintain anisotropic stress, almost no trace of the initial state will remain once the samples become entirely rubbery, as long as the sorption degree at this point is independent of the initial state.

DATA ANALYSIS

In addition to verifying the dimensional changes anticipated in *Figure 3* for the different type of sample, it is also important to examine the sorption rates and swelling transport mechanism since these could be affected by stress profiles within the glassy core. The swelling mechanism was identified through the simple empirical expression[1,11,17]:

$$M_t/M_\infty = kt^n/L_o \qquad (1)$$

where M_t is the mass of solvent absorbed at time t, M_∞ is the mass of solvent absorbed at equilibrium, k is a rate constant, n is the transport exponent and L_0 is the initial sample thickness. The transport exponents were calculated by linear regression using either the portion of the curve prior to the disappearance of the glassy core or for $M_t/M_\infty < 0.6$, whichever is reached first. For a slab or disc, when $n = 0.50$ the process is diffusion-controlled and is termed Fickian or case I transport. Transport is assumed to be relaxation-controlled (case II) when $n = 1.0$. When the exponent n is between 0.5 and 1.0 or if the dimensional dependence deviates from that expressed by equation (1), the transport is termed anomalous. An observation of $n > 1$ is termed super case II.

Table 3 Sorption data from *Figures 5–7*. Differing levels of anisotropic stress do not affect the transport mechanism or diffusion coefficient. The ratios A_0/A_a and L_a/L_b are nearly equal for each sample, as expected

Type	Transport exponent n	Diffusion coefficient D (10^7 cm^2 s^{-1})	Swelling ratio q	A_0/A_a	L_a/L_b
1	0.50 ± 0.01[a]	1.4 ± 0.1	1.55 ± 0.01	0.90 ± 0.02	0.96 ± 0.01
2	0.50 ± 0.01	1.4 ± 0.1	1.55 ± 0.01	0.99 ± 0.02	1.00 ± 0.01
3	0.50 ± 0.01	1.2 ± 0.1	1.55 ± 0.01	1.14 ± 0.02	1.09 ± 0.02
3^+	0.50 ± 0.01	1.5 ± 0.2	1.54 ± 0.01	1.99 ± 0.04	1.81 ± 0.07

[a] 95% confidence intervals

Table 4 Sorption data from *Figure 8*. Anomalous methanol transport in glassy PHEMA is observed, but the dimensional dependence of equation (1) holds well (implied by the nearly constant values of n and k)

Initial thickness (mm)	Transport exponent n	log (k)	Swelling ratio q	A_0/A_a	L_a/L_b
0.60 ± 0.03	0.71 ± 0.06[a]	−1.46	2.34 ± 0.02	0.68 ± 0.02	0.79 ± 0.04
0.77 ± 0.02	0.68 ± 0.02	−1.56	2.35 ± 0.02	0.63 ± 0.03	0.77 ± 0.06
1.13 ± 0.01	0.63 ± 0.01	−1.67	2.36 ± 0.02	0.65 ± 0.02	0.78 ± 0.05
1.30 ± 0.02	0.63 ± 0.01	−1.71	2.34 ± 0.02	0.67 ± 0.02	0.78 ± 0.04

[a] 95% confidence intervals

Table 5 Sorption data from *Figures 9* and *10*. Differing levels of anisotropic stress have little effect on the transport mechanism and rate constant. The ratios A_0/A_a and L_a/L_b are nearly equal for each sample, consistent with the data in *Table 4*

Type	Transport exponent n	log (k)	Swelling ratio q	A_0/A_a	L_a/L_b
1	0.63 ± 0.01[a]	−1.50	2.43 ± 0.02	0.55 ± 0.01	0.62 ± 0.07
2	0.54 ± 0.04	−1.26	2.36 ± 0.02	1.03 ± 0.02	1.00 ± 0.01

[a] 95% confidence intervals

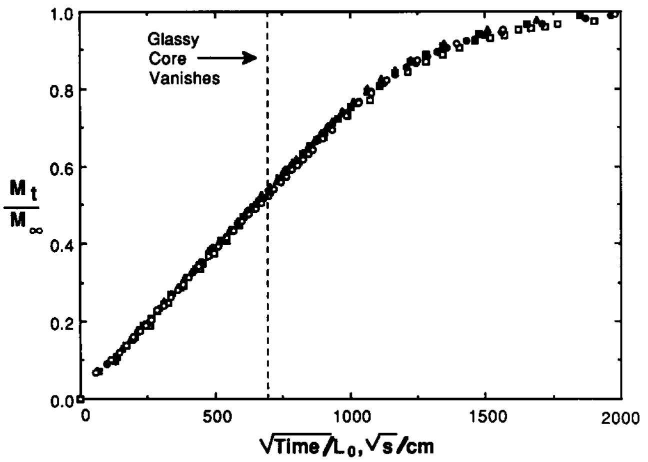

Figure 4 Water sorption kinetics of type 3 PHEMA samples as a function of thickness. A single, initially linear master curve when sorption is plotted against the square root of time indicates a Fickian transport mechanism. Initial thickness (mm): □, 0.60; ●, 0.78; ■, 1.14; ▲, 1.25; ○, 1.35

For cases of Fickian transport, a diffusion coefficient can be extracted from the kinetic coefficient k, or by using the following expression with a non-linear least squares fit over the same interval of M_t/M_∞ used to extract n[11,17]:

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} [8/(2n+1)^2\pi^2] \times \exp[-(2n+1)^2\pi^2(Dt/L_0^2)] \qquad (2)$$

where D is the diffusion coefficient in a polymer-fixed reference frame. Although the precise meaning of this diffusion coefficient is debatable in this context, it is more meaningful even as an empirical rate constant than a value of the rate constant k would be.

EXPERIMENTAL

Polymer synthesis

2-Hydroxyethyl methacrylate (HEMA) monomer (Aldrich Chemical Co., 97% purity) was further purified by vacuum distillation at 67°C and 467 Pa; the middle 60% of the distillate was used. Cuprous chloride was added to inhibit polymerization during distillation. Benzoyl peroxide (0.5 wt%, Aldrich) was added as initiator. The solution was deaerated for 15 min in a desiccator and then injected between polypropylene moulds separated with silicone rubber spacers of 1.50 mm thickness. The polymerization was carried out at 60°C for 24 h. A transparent, glassy poly(HEMA) (PHEMA) sheet was obtained and removed from the mould.

Sample preparation

Square samples with aspect ratios (length/thickness) greater than 10 were cut from the central portion of the glassy sheet using a heated razor blade. Samples were then prepared with different stress distributions within the glassy polymer, corresponding to types 1–3 in *Table 1*. The preparation of these samples for water and methanol sorption experiments are described below.

For water sorption experiments. Isotropic, stress-free samples were prepared as examples of type 1 behaviour

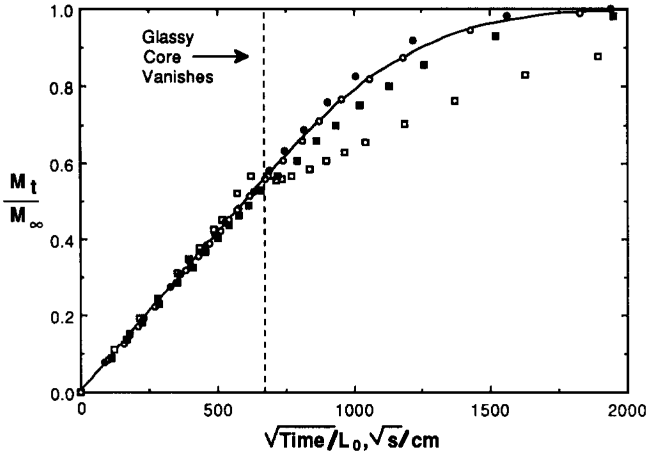

Figure 5 Water sorption kinetics of PHEMA sheets prepared with various levels of deformation and anisotropic stresses in the initial glassy state. Significant differences in sorption kinetics are observed after the disappearance of the glassy core, although the differences in stress do not affect the kinetics prior to this. ●, Type 1; ○, type 2; ■, type 3; □, type 3^+; —, Fickian curve

by first equilibrating them in distilled water, then drying them slowly and isotropically in a vacuum oven (Napco, Model 5831) at 60°C and 1330 Pa for 48 h. Two kinds of type 3 sample were prepared with different levels of anisotropic stress. In one case, the sample was initially equilibrated in water, then dried at constant area using a gel dryer (Bio-Rad Model 543) at 60°C and 467 Pa for 36 h. A type 3 sample with an even greater level of anisotropy was prepared by first equilibrating the sample in a 50 vol% ethanol–water solution, which is a much better solvent for PHEMA than pure water ($q \approx 3.6$ in this solution while $q \approx 1.6$ in pure water; q = swollen weight/dry weight). This gel was then dried at constant area in the gel dryer, first at 24°C and 467 Pa for 3 days and then at 60°C and 467 Pa for 4 days. The slow drying of this highly swollen sample was required to prevent crazing and cracking of the sample. Because of the high swelling degree of PHEMA in the ethanol–water solution, this sample area was much extended relative to the isotropic case and thus contained the greatest tensile stress in the direction of thickness and the greatest compressive stress perpendicular to this; it will be referred to as type 3^+ to distinguish it from samples dried from equilibrium swelling in water. A type 2 sample was prepared by equilibrating the sample with water, then drying it isotropically at 24°C until the sample just started to become glassy and the area was nearly equal to A_a. It was then placed in the gel dryer and dried by the slow process described above.

For methanol sorption experiments. Two kinds of type 1 sample were prepared containing different stress levels. The first set of samples were exactly the same as the type 1 samples described above. The other set of type 1 samples were prepared by first equilibrating them in water, followed by drying in the gel dryer at 60°C and 467 Pa for 5 days. Since PHEMA swells much more in methanol than in water ($q \approx 2.4$ *versus* $q \approx 1.6$), $A_0/A_a < 1$, even for these anisotropic samples. A type 2 sample was prepared by equilibration in methanol, isotropic drying until the area reached A_a, followed by the slow constant-area drying process in the gel dryer. A type 3 sample for methanol sorption could not be prepared without crazing and cracking.

Sorption experiments

Gel samples were used within 3 weeks of preparation; dimensions were stable over this time period. The residual solvent content was 3.12 ± 0.08 wt% for all samples. It is virtually impossible for such drying procedures to remove all traces of solvent. However, we have already shown that the drying procedures used here do not significantly alter the kinetics of solvent sorption, even after repeated swell/dry cycles[11].

The dynamic swelling measurements were done by a simple gravimetric method at ambient conditions (T = 24°C). Samples were removed from the solvent at different time intervals, quickly blotted with filter paper, and weighed using a Mettler analytical balance (Model AE 200, ±0.0001 g). The sample dimensions (thickness and area) were measured by a Manostat caliper (±0.1 mm). The time required for a complete set of measurements was less than 20 s in comparison with swelling times on the order of 30 h, so temporary removal from the solvent bath did not affect the kinetics. This procedure was followed until equilibrium was clearly established.

RESULTS AND DISCUSSION

Since PHEMA samples prepared by the different techniques necessarily have different thicknesses prior to the sorption experiments, it is important to establish the dimensional dependence of the swelling process using equation (1) in order to interpret the results. To do this, PHEMA sheets of different thicknesses were swollen in water, then dried in the gel dryer as described in the previous section, producing type 3 samples of different thicknesses. *Figure 4* clearly shows that the dimensional effect on water sorption kinetics can be eliminated by using ($t^{1/2}/L_0$) as the time variable: a single master curve is produced which is independent of the initial thickness. *Table 2* lists the results of the analysis of the data in *Figure 4*; the swelling mechanism of PHEMA is clearly Fickian, as it is for initially stress-free type 1 samples[11].

Using ($t^{1/2}/L_0$) as the time variable, *Figures 5, 6* and 7 show the changes as a function of time in mass, thickness and area, respectively, for PHEMA samples prepared as types 1, 2, 3 and 3^+ according to the techniques described above. It is readily seen that all of

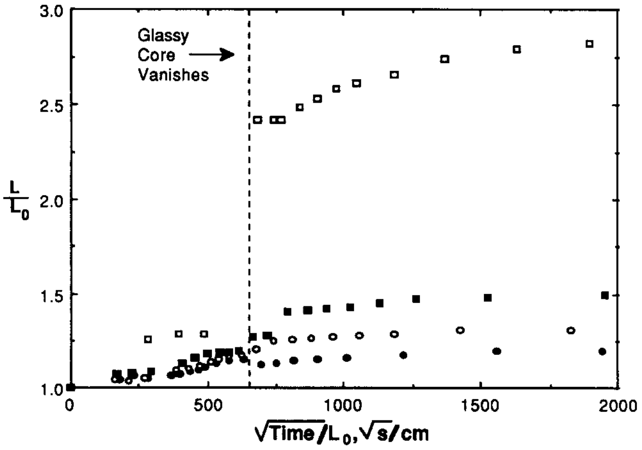

Figure 6 Changes in thickness of PHEMA sheets swelling in water for samples prepared with various levels of deformation and anisotropic stress in the initial glassy state. The changes described in *Table 1* are observed. ●, Type 1; ○, type 2; ■, type 3; □, type 3^+

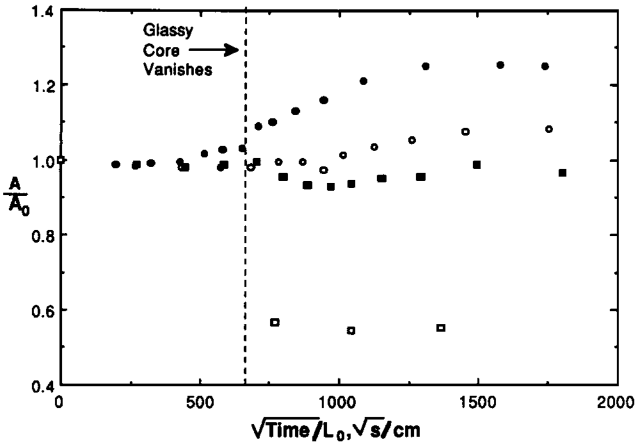

Figure 7 Changes in area of PHEMA sheets swelling in water for samples prepared with various levels of deformation and anisotropic stress in the initial glassy state. The changes described in *Table 1* are observed. ●, Type 1; ○, type 2; ■, type 3; □, type 3$^+$

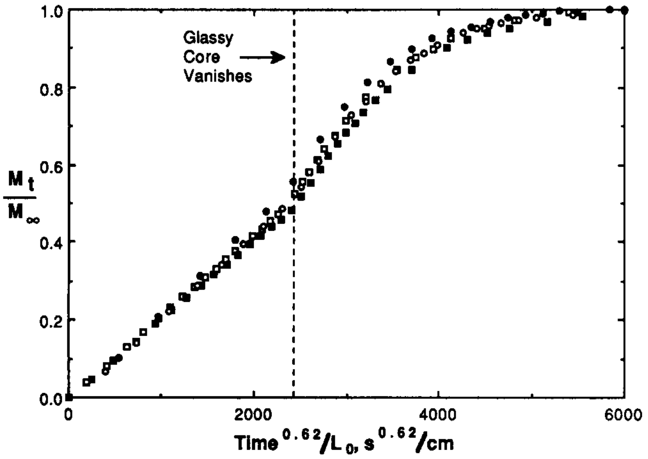

Figure 8 Methanol sorption kinetics as a function of thickness for type 1 PHEMA sheets prepared with modest anisotropic stresses in the initial glassy state. The development of a single master curve as plotted indicates the validity of the dimensional dependence assumed in equation (1), even though the transport mechanism is anomalous. Initial thickness (mm): □, 1.30; ■, 1.13; ○, 0.77; ●, 0.60

the qualitative predictions of *Table 1* are confirmed experimentally for this polymer/solvent system. Note in particular the dramatic changes in area and thickness that occur when the glassy core vanishes for the type 3$^+$ sample, the nearly perfect fit of a type 2 sample to the Fickian transport equation at all times, and the nearly constant area maintained by a type 3 sample over the entire course of the sorption process. Despite the substantially different levels of anisotropic stress incorporated into the polymer samples by the different preparation techniques, *Table 3* shows that no differences in the transport mechanism, *n*, kinetics, *D*, or equilibrium swelling ratio were observed. Also as expected, for each sample the ratios A_0/A_a and L_a/L_b are nearly equal. Furthermore, *Figure 5* indicates that the value of M_t/M_∞ at the disappearance of the glassy core is not significantly influenced by the level of initial anisotropic stress.

We also wished to examine these phenomena for a non-Fickian system, so the previously described experiments were repeated for methanol, which has a transport exponent of approximately 0.62 for stress-free type 1 samples[18]. Again, the dimensional dependence of the sorption process was first tested (using the slightly anisotropic type 1 samples described earlier), and it was consistent with equation (1), as shown in *Figure 8*. The parameters obtained from this data are summarized in *Table 4*. No significant variation with thickness was observed for any of the parameters.

Using $t^{0.62}/L_0$ as the time variable, *Figures 9* and *10* show the changes as a function of time in mass and thickness, respectively, for PHEMA samples prepared as initially stress-free type 1 and as type 2 according to the techniques described in the previous section (the data in *Figure 8* may also be directly compared with those in *Figure 9*). The parameters extracted from this data are summarized in *Table 5*. Again, all of the qualitative predictions of *Table 1* are confirmed experimentally for the methanol–PHEMA system.

CONCLUSIONS

The key parameter used to anticipate the direction and the extent of the dimensional rearrangements and the change in the sorption rate when the glassy core vanishes is the ratio A_0/A_a. The magnitude of these changes increases as this ratio deviates from unity. For a given

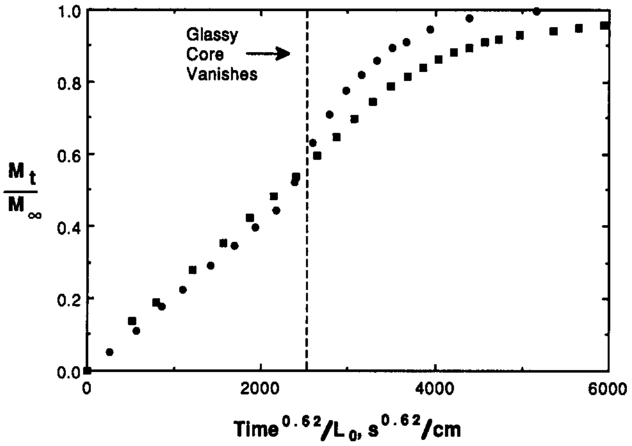

Figure 9 Methanol sorption kinetics of PHEMA sheets prepared with differing levels of anisotropic stresses in the initial glassy state. Significant differences in sorption kinetics are observed after the disappearance of the glassy core, although the differences in stress have a minor effect on the kinetics prior to this. ●, Type 1; ■, type 2

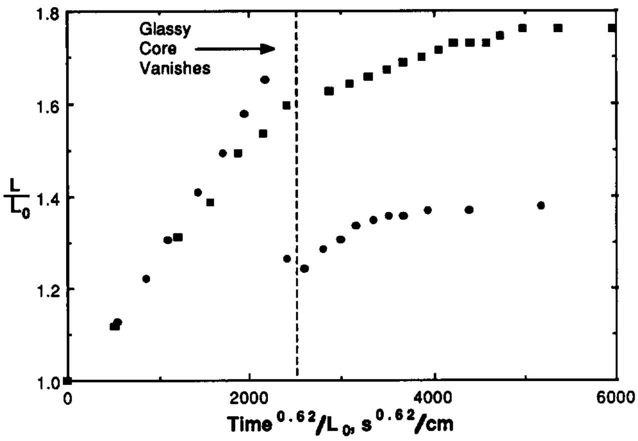

Figure 10 Changes in thickness of PHEMA sheets swelling in methanol for samples prepared with differing levels of stress in the initial glassy state. The changes described in *Table 1* are observed. ●, Type 1; ■, type 2

solvent, these changes can be controlled by incorporating anisotropic stresses into the glassy polymer by controlled deformation of the sample. The existence of these stresses did not significantly affect the swelling mechanism or the rate constants. The magnitude of the dimensional rearrangements at the disappearance of the glassy core increased with increasing swelling degree in the solvent.

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