Volume change kinetics of temperature-sensitive poly(vinyl methyl ether) gel

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Thermally responsive gels of poly(vinyl methyl ether) (PVME) were formed by the γ-irradiation of solutions of linear PVME. Under precisely defined synthesis conditions, the shrinking rates of the gels could be increased to values well above the range observed for gels formed by copolymerization/crosslinking reactions. This enhancement in rate appears related to the development of a microporous structure which allows the convective expulsion of solvent from the network; this occurs more quickly than the diffusive motion of the network. The overall rate of a cyclical process using responsive gels can also be enhanced if one stage of the process, either swelling or shrinking, is reversed before equilibrium is achieved.

(Keywords: diffusion; sorption; syneresis; responsive gel; hydrogel; poly(vinyl methyl ether))

INTRODUCTION

Many different classes of crosslinked polymer gels display phase transitions, i.e. abrupt changes in swollen volume in response to small environmental changes like pH, temperature, light intensity, electric field, ionic strength and even specific stimuli like glucose concentration. In the past several years, interest in such gels has increased sharply as new applications have been proposed which exploit this phenomenon. For drug delivery devices the gel might be used to displace a solution from a reservoir by expansion, control solute flux through a gel membrane or regulate the release rate of a drug embedded in the gel matrix – all in response to an environmental stimulus[1–4]. Responsive gels have also been used to dewater protein solutions, coal slurry and waste sludge[5–8]. Environmentally responsive gels can also be used as mechano-chemical actuators and switches. To demonstrate the potential use of such gels in robotics, Shiga *et al.* demonstrated that 'fingers' made from electrical field-sensitive ionic poly(vinyl alcohol)-based gels can lift irregular objects[9].

The most widely studied responsive polymer gels have been acrylamide copolymers and derivatives like *N*-isopropylacrylamide, formed by free radical copolymerization/crosslinking reactions. Temperature-sensitive gels in particular are readily formed by crosslinking polymers which display lower critical solution temperatures, such as poly(*N*-isopropylacrylamide) (PNIPAAm), poly(vinyl acetate-*co*-vinyl alcohol), and poly(vinyl methyl ether) (PVME)[10]. Kinetic data reported in the literature show that the rate of volume change for these gels is very slow; for example, it takes more than a day for a sheet of PNIPAAm gel 1 mm thick to swell or shrink to equilibrium[4,7,11]. This slow response undermines the potential of these gels in most applications where a quick response is desirable (e.g. mechano-chemical actuators or switches). Even where response time is less critical, slow response can be detrimental to the economic viability of an application[12].

However, a report by Huang *et al.* briefly described a radiochemically crosslinked PVME gel which appeared to swell and shrink in response to changes in temperature (swelling below 310 K, shrinking above it), orders of magnitude faster than previously reported responsive gels, mostly solution polymerized polyacrylamide derivatives[13]. They synthesized a PVME gel by irradiating a 30 wt% PVME solution mixed with 15 wt% ferric oxide powder (the ferric oxide was added to increase the thermal conductivity of the gel and minimize heat transfer limitations) with γ-rays from a ^{60}Co source for 9.3 h at an intensity of 1.09 Mrad h^{-1}. The fast response of these gels was ascribed to a microporous structure caused by phase separation of the polymer solution during irradiation[14,15].

In this project, we synthesized PVME gels following a similar procedure, but varied radiation dose and intensity to study their effect on the swelling/shrinking properties of PVME gel. These gels were characterized by studying their equilibrium and dynamic volume change in response to the change in temperature.

DATA ANALYSIS

The solvent sorption kinetics of both responsive and ordinary polymer gels has been studied for over 20 years. Nonetheless, a single standard method for treating the kinetic data has not been widely accepted due to the diverse, complex sorption phenomena which can be observed in different systems, e.g. moving solvent fronts, two-stage sorption curves and equilibrium overshoots[16,17].

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Perhaps the most widely used means of analysing such data is to fit the first 60% of the sorption data to the following simple empirical equation[16]:

$$M_t/M_\infty = kt^n \tag{1}$$

where M_t is the mass absorbed or desorbed at time t, M_∞ is the mass absorbed or desorbed at equilibrium ($t = +\infty$), k is an empirical rate constant and n is an empirical number called the transport exponent. A value of 0.5 for the transport exponent is indicative of a diffusion-controlled process. The difficulty in using this equation to compare rates of sorption and desorption for different materials is that the rate constant k depends upon the transport exponent n, so that a direct comparison of k values is possible only if the materials have the same value of the transport exponent.

Rather than fitting data to any kind of model, empirical or otherwise, some authors simply state the amount of time required for a gel to reach some percentage of its equilibrium mass or volume. However, this time can be misleading because some samples may display an initially rapid volume change followed by a very slow drift to the final equilibrium value, while others may proceed at a more uniform rate. Furthermore, equilibration time is strongly thickness-dependent. In fact, for a diffusion-controlled process, the equilibration time scales with the square of the characteristic dimension.

However, the swelling and deswelling of rubbery polymer gels, including responsive polymer gels, often occurs by a relatively simple diffusion-controlled process. In such cases, the response kinetics can be characterized by a single parameter. This parameter is a diffusion coefficient which can be obtained from the solution of Fick's law of diffusion with a polymer-fixed frame of reference (that is, a reference frame that moves with the polymer as it expands or contracts) with the appropriate boundary conditions. In the polymer-fixed reference frame, the mathematics are equivalent to the constant volume problem, which greatly simplifies the solution of the problem[18–20]. For planar geometry, the polymer-fixed reference frame diffusion coefficient D_p can be calculated from the following equation (for sheets with aspect ratios greater than 10:1)[18]:

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} [8/(2n+1)^2\pi^2] \times \exp[-(2n+1)^2\pi^2(D_p t/L^2)] \tag{2}$$

where L is the initial thickness of the sheet. An analogous equation in terms of the normalized approach to equilibrium dimension L_t/L_∞ can also be derived using the approach of Tanaka and Fillmore, which starts with the equations of motion rather than Fick's law[21]. For homogeneous, rubbery gels, the values of the diffusion coefficients obtained by either method have been observed[7,21–23] to lie within the range of 0.1×10^{-7} to 8×10^{-7} cm^2 s^{-1}. These values are not significantly dependent upon the theory used to calculate them or corrections that can be made to adjust for the differences in reference frame, except for very large changes in swelling degree[19,20].

However, deviations from equation (2) can be expected if any of the underlying assumptions in its development are violated. Specifically, the diffusion coefficient is assumed to be independent of position within the gel and concentration, the surface concentration is assumed to reach the equilibrium value instantaneously, and non-diffusive fluxes (i.e. convection) and rate-limiting steps (e.g. heat transfer) are assumed to be absent. Thus in many cases, deviations from eqnation (2) may be expected[19,24,25].

Nonetheless, a best-fit diffusion coefficient can still be a useful means of comparing the volume change kinetics of disparate gel samples, especially if the deviation from equation (2) is not too severe. First of all, the value of a diffusion coefficient is thickness-independent (thickness-dependent anomalies aside) and its magnitude has intuitive meaning, unlike the purely empirical constants of equation (1). Secondly, the characteristic time-dependence of diffusive processes is well known by a diverse body of scientists. Describing the rate of a non-diffusive process by direct comparison to a diffusive process occurring at a comparable average rate (i.e. a purely diffusive process occurring with the best-fit diffusion coefficient) aids comparison of data from diverse systems. Thus it is our opinion that a best-fit diffusion coefficient provides a good basis for making rate comparisons of widely different gels even when deviations from equation (2) are observed. Of course, the best alternative method to enable in-depth comparisons is to provide the entire set of kinetic data, but this is often not practicable; some form of data reduction is required.

Thus to make rate comparisons of different gels, the best-fit value of D_p to the sorption/desorption data was evaluated by fitting the weight change data to equation (2) using a non-linear least-squares fit. This was done using Marquardt's algorithm for non-linear regression[26] and the best-fit value of D_p was obtained from a plot of the fractional approach to equilibrium M_t/M_∞ as a function of $t^{1/2}/L$.

EXPERIMENTAL

Synthesis

PVME gels were synthesized by γ-irradiation at ambient conditions of 30 wt% PVME solutions (diluted with distilled water from a 50 wt% aqueous solution obtained from Aldrich Chemical Co.; PVME weight average molecular weight ≈90000) containing 15 wt% ferric oxide (Fe_3O_4) (Fisher Scientific Co.) using the ^{60}Co source in the College of Engineering at the University of Cincinnati. These solutions were degassed, poured into glass vials (15 mm i.d., 17 mm o.d.) and sealed for irradiation. Gels with different properties were obtained by varying the radiation dose and intensity from 5.0 to 16.9 Mrad and 0.24 to 0.85 Mrad h^{-1}, respectively. Polymer solutions irradiated with γ-rays for a total dose of less than 5 Mrad did not gel. After irradiation, the glass vials were carefully broken and cylindrical rods of gel were removed. Discs of uniform thickness ($\pm$0.03 mm) were obtained by slicing the swollen cylindrical gel samples with a razor blade. For detailed examination of the volume change kinetics, PVME gel sheets were prepared by irradiating PVME solution sandwiched between two glass plates (2.2 mm thick) separated by silicon rubber gaskets (0.8 mm thick); the mould was taken apart after irradiation to recover a flat sheet of gel. Square samples with aspect ratios greater than 10:1 were cut from the central part of the sheet. While basically homogeneous macroscopically, the gels had some gas bubbles in them, sometimes as large as 1 mm in diameter.

Table 1 Synthesis conditions and equilibrium swelling degrees of PVME gels with 30 wt% PVME and 15 wt% ferric oxide in the aqueous pregel solution

Trial number	Radiation intensity (Mrad h^{-1})	Radiation time (h)	Total dose (Mrad)	Swelling ratio at 23°C (swollen wt/dry wt)
1	0.24 ± 0.01	24.6	5.9 ± 0.2	13.3 ± 0.3
2	0.24 ± 0.01	34.2	8.2 ± 0.4	5.7 ± 0.1
3	0.24 ± 0.01	49.8	12.0 ± 0.5	5.4 ± 0.1
4	0.85 ± 0.115	13.0	11.1 ± 1.5	5.4 ± 0.1

These bubbles apparently formed from the gases generated during the γ-irradiation. The ferric oxide was a fine powder that did not settle during γ-irradiation due to the high viscosity of the 30 wt% PVME solution. It was added to the polymer solution as an inert material which would increase the thermal conductivity of the resulting gels and make them opaque under the microscope. Gels could also be formed in the absence of the ferric oxide, but this was not studied extensively.

All PVME gels were swollen in distilled water at 23.0 ± 0.1°C and then shrunken at 50 ± 0.1°C to leach out the sol fraction over at least a week. At 50°C, the water in which gel was immersed became cloudy, indicating that a sol fraction was diffusing out of the gel. After several such swell/shrink cycles, no further sol fraction leached out, and the gels were considered ready for testing.

Swelling measurements

The PVME gels synthesized were characterized by their equilibrium degrees of swelling (swollen mass/dry mass) and rates of volume change. Most swelling measurements were made by a simple gravimetric method. A gel sample equilibrated with water at a given temperature was placed in a vial of distilled water, which was then immersed in a constant temperature bath (± 0.1°C). The polymer sample was removed from the water at appropriate intervals, blotted free of surface water with absorbent paper and weighed using an analytical balance (± 0.0001 g). This procedure was carried out until the sample attained constant weight. Linear dimensions were measured with a micrometer caliper (accuracy ± 0.01 mm) and a vernier caliper (accuracy ± 0.1 mm).

Although the gravimetric method described above was simple and gave highly reproducible results ($\pm 2\%$), in some cases the rate of volume change was too fast to accurately measure the swelling kinetics by this method. For these samples, the videomicroscope system was used to obtain kinetic data. The sample being studied was placed in a beaker of water which was then immersed in a transparent plastic water container on the stage under a microscope (Olmypus model SZH-ILLD). The water temperature in the plastic container was kept constant by circulating water from the constant temperature bath. Images of the gels were taken every 5 s using a TV camera mounted on the microscope; they were digitized and analysed using IMAGE image analysis software*. This analysis determined the area and the linear dimensions of the sample as a function of time and, since these gels swelled and shrank isotropically, the gel volumes could be calculated. The data obtained from this experiment were analysed in the same way as those obtained from the gravimetric experiments.

Another advantage of the videomicroscope set-up is that the gels do not need to be removed from the water bath for measurement. This eliminates warming/cooling cycles between bath and room temperatures during mass measurements. Heat transfer is so much faster than mass transfer in most gels that this does not disturb the kinetic measurements, except when the response is so fast that use of the videomicroscope is required anyway[27].

RESULTS

Equilibrium swelling

The gel swelling ratio (swollen weight/dry weight) decreases with an increase in the total radiation dose at constant radiation intensity as shown in *Table 1*. This is consistent with an increase in network crosslinking density as the radiation dose increases. The gels of trial 1, formed by crosslinking at a low radiation intensity (0.24 Mrad h^{-1}) and total dose (6 Mrad) shrank at very high rates. However, they were weak and could not maintain their dimensions when removed from water for accurate measurement of the rates. After repeating 10–15 swell/shrink cycles, trial 1 gels disintegrated. Similar results were observed for ferric oxide-free PVME gel crosslinked by 9.6 Mrad of radiation with γ-rays of intensity 0.29 Mrad h^{-1}. However, the gels from trials 2–4 were stable, maintaining consistent dimensions even when swollen and shrunken repeatedly over 3 months. The temperature dependence of the swelling ratio for trial 4 PVME gel is shown in *Figure 1*; a sharp volume transition at 37°C is the key feature.

Swelling kinetics

A PVME gel sheet from trial 4 was equilibrated at 34°C, then immersed in water at 26°C, causing the gel to swell without crossing the volume transition at 37°C (because the thermal conductivity is several orders of magnitude greater than the mass diffusivity of this process, the swelling process occurs nearly isothermally at the final temperature). As shown in *Figure 2*, the volume change matches the classical diffusion curve

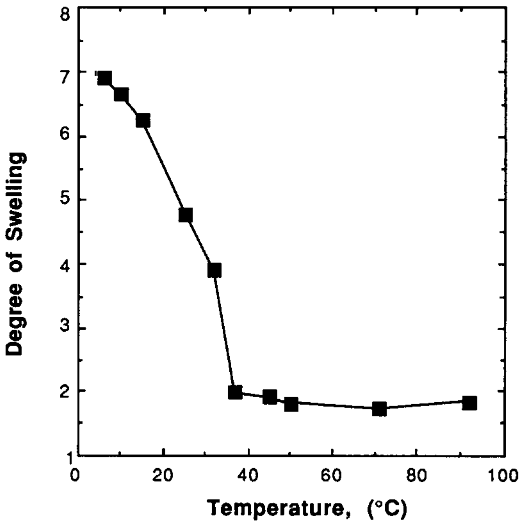

Figure 1 Equilibrium degree of swelling of PVME gel (trial 4) at different temperatures

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*IMAGE software is written by W. Rasband, NIH, Bethesda, MD, USA and is available in Macintosh user group libraries (equation (2)) over the entire range with a high yet typical magnitude of diffusion coefficient. However, the reverse of this process, shrinking at 33°C after equilibration at 26°C, occurs with a best-fit diffusion coefficient more than an order of magnitude larger than swelling. Slight deviation from the Fickian curve – a slower shrinking rate over the last portion of the curve – shows that this is not a simple diffusive process. However, the key point is that the shrinking rate for this gel is much greater than for conventional gels, yet these gels are strong enough to resist any deterioration in structure. Surface bubbles or blisters do not appear on the surface of the gel when shrinking, as is often observed for conventionally prepared PNIPAAm gels, but the PVME gels stiffen quickly as PNIPAAm gels do when warmed above the transition temperature.

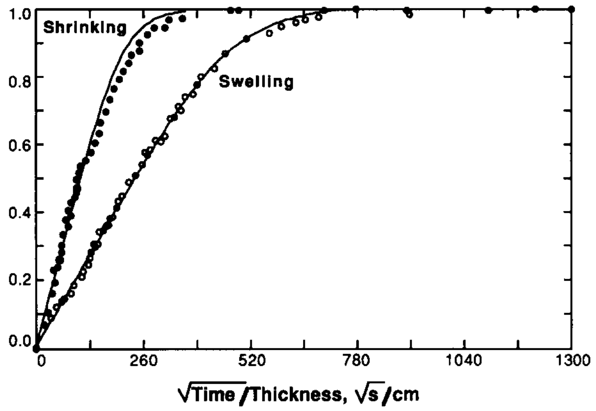

Figure 2 Volume change kinetics of PVME gel (trial 4) between two states below the volume transition of 37°C. Swelling fits Fick's law but shrinking deviates slightly: ○, swelling (from 33 to 26°C), $D_p = 7.3 \times 10^{-7}$ cm^2 s^{-1}; ●, shrinking (from 24 to 34°C), $D_p = 8.5 \times 10^{-6}$ cm^2 s^{-1}

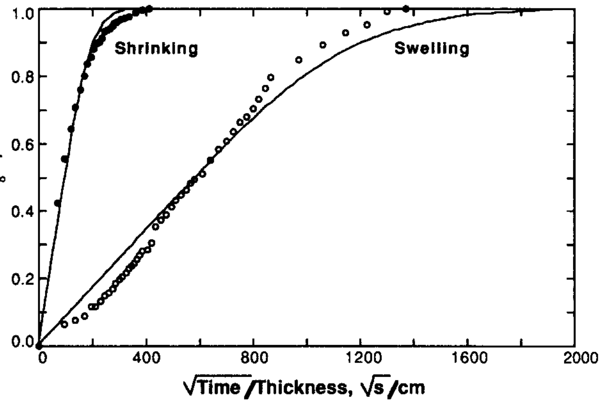

Figure 3 Volume change kinetics of PVME gel (trial 4) between states above and below the volume transition of 37°C. Non-Fickian behaviour is observed for both swelling and shrinking: ○, swelling (from 50 to 24°C), $D_p = 4.0 \times 10^{-7}$ cm^2 s^{-1}; ●, shrinking (from 23 to 50°C), $D_p = 1 \times 10^{-5}$ cm^2 s^{-1}

When a gel from trial 4 is caused to swell or shrink across the transition temperature of 37°C, both swelling and shrinking deviate significantly from Fickian behaviour. As shown in *Figure 3*, the swelling curve is sigmoidal when plotted against the square root of time and the shrinking curve shows a distinctly slower second stage as equilibrium is approached. However, the best-fit diffusion coefficients for both shrinking and swelling across the volume transition are comparable to those obtained when the transition is not crossed.

The swell/shrink kinetics of PVME gels from trial 3, prepared by crosslinking linear PVME at a lower radiation intensity than trial 4 but approximately the same total dose, were also examined. The shrinking rate for trial 3 gels is much slower than that observed for gels from trial 4, and occurs at rates comparable to conventionally prepared gels. The data from all these kinetic experiments are given in *Table 2*. The values of diffusion coefficients given in this table are calculated from a non-linear least-squares fit of experimental data to equation (2).

DISCUSSION

As indicated in *Table 2*, only for swelling between states below the transition temperature do the volume change kinetics of PVME gel fit the diffusion curve well. The deviations from the diffusion equation observed when swelling or shrinking occurs across the volume transition are very similar to those reported for conventionally prepared, solution-polymerized PNIPAAm gels when the transition temperature is crossed.[11,25]. We have recently observed the same deviations for PNIPAAm gels undergoing both solvent- and salt-induced transitions[28]. Specifically, the shrinking rate is observed to slow significantly in the terminal stages of shrinking, causing the observed shrinking rate to fall below the theoretical diffusion curve that fits the first stage of the curve. For PNIPAAm gel, Matsuo and Tanaka have suggested that this phenomenon may occur due to the formation of a dense skin on the gel surface as the gel shrinks, temporarily restricting the movement of solvent out of the gel[25]. In contrast to the shrinking behaviour, the volume change curve for swelling across the phase transition for gels is sigmoidal when plotted against the square root of time. This could be due to an initially

Table 2 Swelling and shrinking data for PVME gel in water at different temperatures. For non-Fickian kinetics, D_p is simply an empirical constant indicating the rate at which a pure diffusion process would have to proceed to most closely match the actual data. *Figure 3* displays the strongest deviations from equation (2) observed

Trial number	$T_1 \Rightarrow T_2$ (°C) swelling or shrinking	Initial thickness (mm)	Final wt/ initial wt	D_p (10^7 cm^2 s^{-1})	Type of sorption curve
4	$24 \Rightarrow 50$ Shrinking	1.0 ± 0.03	0.24 ± 0.02	100.0 ± 7.5	Two-stage
4	$50 \Rightarrow 24$ Swelling	0.8 ± 0.03	4.17 ± 0.1	4.0 ± 1.8	Sigmoidal
4	$24 \Rightarrow 34$ Shrinking	1.1 ± 0.03	0.30 ± 0.02	85 ± 6	Two-stage
4	$33 \Rightarrow 26$ Swelling	0.9 ± 0.03	3.38 ± 0.1	7.3 ± 0.5	Fickian
3	$23 \Rightarrow 50$ Shrinking	1.0 ± 0.03	0.25 ± 0.02	4.0 ± 3.4	Two-stage
3	$50 \Rightarrow 23$ Swelling	0.76 ± 0.03	3.58 ± 0.1	2.7 ± 0.7	Sigmoidal

retarded swelling rate caused by the initially low water content of the collapsed gel and the dominance of the polymer–polymer interactions in this state. This type of behaviour can also be successfully modelled using the Long and Richman surface relaxation model, which assumes that the surface of the polymer only slowly reaches the equilibrium degree of swelling[29]. Thus these observed deviations from simple diffusive processes seem to be characteristic of a broad range of environmentally responsive gels when they are swollen or shrunken across the volume transition point. This appears to be true even though the trial 4 PVME gels shrink at a rate that appears to be much too fast to be simply explained in terms of deviation from diffusion control.

However, if a gel sample had a heterogeneous microstructure, the characteristic length for the diffusive rearrangement of the polymer network would be that characteristic of the microstructure rather than the macroscopic dimension of the sample. Since diffusion time is proportional to the square of the dimension, reducing the diffusion path from millimetres to micrometres reduces the diffusion time by a factor of 10^6. Thus in a heterogeneous gel, the rate limiting step for mass transfer is likely to be the convective expulsion of water from micropores within the gel, rather than the diffusive rearrangement of polymer chains in the solvent, as is the case for homogeneous gels like PNIPAAm. Differences in rates observed for gels prepared differently may then be related to the degree of interconnectivity of pores which develop within the gel during synthesis. In principle, interconnected pores would be needed to allow water to be readily expelled from pores by a convective process instead of the slower diffusive process normally observed for homogeneous gels. It is known that open cell foams, which have an interconnected porous structure, have water vapour permeabilities two orders of magnitude higher than closed cell foams[30]. This picture of the microstructure of such fast-response gels might also lead to an understanding of the asymmetry in the swelling and shrinking rates of the gels. In this light, it is somewhat surprising that the diffusion equation fits some of the data quite well.

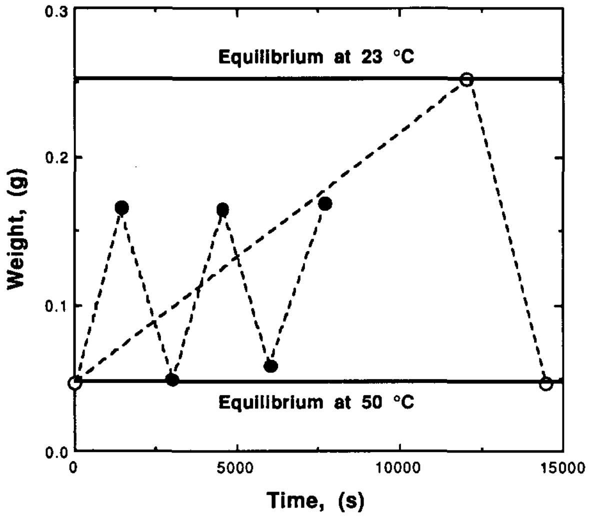

Figure 4 A gel sheet (trial 4 gel, initial thickness 0.08 cm) is alternately warmed and cooled to induce swell/shrink cycles. Stopping short of the equilibrium state on one leg of the cycle results in a sustainable process with a much greater cycling frequency than a process which always approaches equilibrium before the cycle is reversed

There is some evidence for assuming the primacy of the physical structure of the gel in determining the accelerated shrinking rates observed for trial 4 gels. This includes the fact that the gels from trial 4 had identical chemical compositions, total radiation doses and the same swelling degrees as the trial 3 gels, yet the best fit shrinking diffusion coefficients differed by nearly a factor of 20, while the swelling diffusion coefficients were virtually identical. Although these gels are indistinguishable on a macroscopic basis, they must have different microstructures. Scanning electron micrographs indicate the presence of a complex structure with micrometre-scale features in the PVME gels which are not observed in micrographs of solution-polymerized PNIPAAm gels, although sample preparation artifacts cloud this conclusion (it is difficult to freeze highly swollen gels in preparation for microscopy without altering the original structure). The fast response of PVME gels was also attributed by Morishita *et al.* to such a highly macroporous structure; they postulated that temperature-induced phase separation is required to develop fast-response gels[15]. It is possible that the higher radiation intensity used in trial 4 may have heated the solution enough to cause microsyneresis which was subsequently locked in by further radiation-induced crosslinking; this may not have happened during trial 3. Further evidence of the importance of the physical structure of the gel is that although prepared in a manner virtually identical to that reported by Huang *et al.*, trial 4 gels shrink and swell at dramatically slower rates than observed by that group[13]. This disparity in rates of volume change of chemically identical gels crosslinked under very similar conditions can be explained either by differences in the heat transfer characteristics of the irradiation chamber, which might have led to microsyneresis during irradiation, or else by different physical characteristics (average molecular weight and molecular weight distribution) of the linear polymer precursor[14,15]. To confirm these hypotheses, work is underway with gel systems whose phase separation is easier to control.

Some applications proposed for responsive polymer gels, such as recyclable absorbents, require that the gels be cycled between a swollen and shrunken state as quickly as possible. The synthesis of fast-response gels is a direct answer to this problem. Another approach to minimizing the cycling time is to avoid reaching equilibrium at one end of the cycle, since equilibrium is approached slowly and asymptotically. *Figure 4* demonstrates this principle, showing that many more cycles can be completed and more solution can be processed in a fixed period of time by reversing the swelling process before reaching the equilibrium swollen state. The same principle applies to reversing the shrinking before the equilibrium shrunken state is reached. However, since shrinking is much faster than swelling, enhancement of the overall process would be less dramatic. Note that equilibrium must be achieved on at least one leg of the cycle to make the process sustainable. If both the swelling and shrinking legs of the cycle were reversed before equilibrium at either end was reached, the difference between these two states would steadily decline towards zero. In contrast, the process illustrated in *Figure 4* can be sustained indefinitely.

CONCLUSIONS

Thermally responsive PVME gels can be synthesized by the radiation crosslinking of solutions of the linear polymer. Under precisely defined synthesis conditions, these gels can display volume change kinetics which are much greater than the responsive gels studied over the past decades by numerous research groups. These enhanced kinetics have significant technological importance and demonstrate that a non-diffusive mechanism of solvent transport can be involved in the swelling and shrinking of responsive polymer gels.

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