Mechanical and swelling properties of polyacrylamide gel spheres

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Spheres of crosslinked acrylamide–methylene bisacrylamide copolymer were produced by suspension polymerization. By introducing a vibrating stream of aqueous solution into an organic matrix, particle sizes of 0.33 ± 0.06 to 0.99 ± 0.41 mm in diameter resulted. The swelling of gel spheres in water was compared to that of larger 'bulk' gels, and a significant amount of hydrolysis occurred in the spheres due to the presence of tetramethylethylenediamine (TEMED), used as an initiator. The dependence of the elastic modulus of the gel spheres upon the crosslinker concentration was non-linear, even in the regime where linearity is observed for bulk gels; this appears to be due to the varying amounts of TEMED that diffuses in the spheres and is known to affect the modulus of bulk gels.

(Keywords: elastic modulus; hydrolysis; polyacrylamide gel; equilibrium swelling; suspension polymerization)

INTRODUCTION

The thermodynamic and mechanical properties of polyacrylamide gels have been extensively studied in the past[1–8]. This is undoubtedly due to their interesting characteristics, such as their ability to absorb a large amount of water relative to their weight, the sharp collapse transition exhibited in acetone/water mixtures, and the biocompatibility of the gels. Numerous current and potential applications of acrylamide and substituted acrylamide gels have been suggested, including use in electrophoresis[9,10], use in immobilization and/or controlled release of biological molecules[11–13], use in bioseparations[14], and use for moisture retention in soil[15].

The preparation of polyacrylamide gel spheres, with relatively narrow size distributions and mean diameters of 200 to 1500 μm, and the study of their mechanical and swelling properties is the focus of the present study. Because of their geometry, gel spheres are of interest both for their potential applications and because they are well suited for fundamental studies of the role of surface effects on gel properties. The gel spheres were prepared by introducing a vibrating stream of aqueous monomer/crosslinker solution into a gently stirred organic matrix. The droplets thus created quickly gelled and then slowly settled to the bottom of the reaction vessel. The equilibrium swelling and elastic modulus of the spheres were determined, and were compared to the properties of 'bulk' or 'wall-to-wall' gels prepared in test tubes.

PREPARATION AND PROCEDURE

Preparation of gels

The wall-to-wall gels were prepared using a standard, well established recipe[4,16]. 10 g of acrylamide, 0.266 g of *N*,*N*′-methylene bisacrylamide (BIS) and 0.20 g of ammonium persulphate were added to water to make 100 g of solution. The solution was poured into test tubes and varying amounts of tetramethylethylenediamine (TEMED), used as an initiator, were mixed in. The test tubes were sealed and the polymerization was carried out in a 75 ± 1°C water bath. With the redox couple ammonium persulphate/TEMED, the polymerization could have been carried out at much lower temperatures. However, a temperature of 75°C was selected to match, as closely as possible, the conditions used to prepare the gel spheres. The weight ratio of crosslinking agent to monomer, denoted as C, was varied by changing the amount of BIS added, keeping the amount of all the other ingredients constant.

The spherical gel particles were prepared by suspension polymerization of aqueous monomer solutions in an organic matrix. The aqueous phase, consisting of water, acrylamide, BIS and ammonium persulphate, in the same proportions as in the bulk gel recipe given above, was introduced through a vibrating (60 Hz) syringe needle into a cylindrical column containing the organic phase, a 20% xylene/80% chlorobenzene mixture, containing 0.85 g Span 80, a water-in-oil surfactant, and 0.83 g TEMED per 100 g organic phase. As illustrated in *Figure 1*, the aqueous phase was passed through an ice bath to prevent premature gelation. The needle amplitude was controlled with a variable voltage buzzer. The organic phase was purged with nitrogen for 5 min prior to the addition of the aqueous phase and was maintained at 75 ± 1°C. The xylene/chlorobenzene ratio was selected to obtain a density slightly less than that of the gel particles so that the gel particles would settle upon polymerization. The TEMED was required to produce rapid gelation rates. Without the TEMED, the droplets gelled too slowly, leading to coalescence at the bottom of the reaction vessel. The upper portion of the reaction vessel was kept outside of the water bath. The temperature gradient thus created was sufficient to circulate the particles gently, but not enough to cause excessive coalescence or droplet break-up. After the particles settled, they were removed from the reaction vessel and

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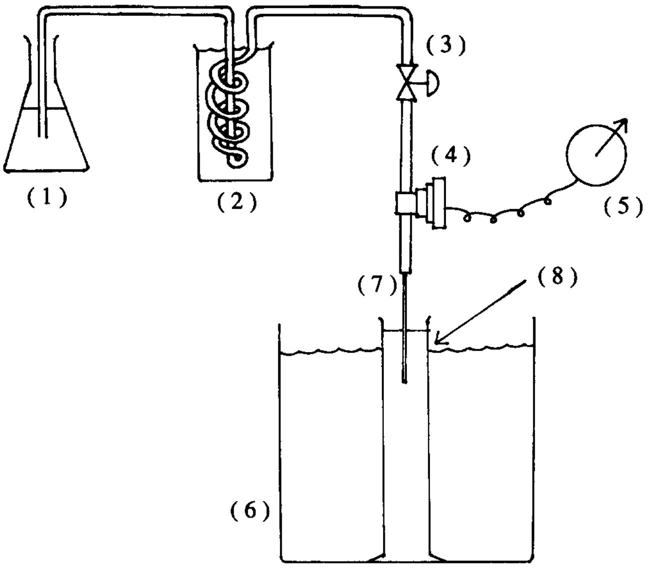

Figure 1 Apparatus for gel sphere production: (1), aqueous phase; (2), ice bath; (3), control valve; (4), buzzer; (5), Variac; (6), water bath; (7), needle; and (8), organic phase (reaction column)

transferred to surfactant-free xylene. This was necessary to prevent water from being leached out of the particles.

The recipe was varied to achieve different crosslink densities, just as in the bulk gel preparation. Particle size was controlled by varying the flow rate of the aqueous phase and controlling the amplitude of the needle vibration. Within experimental error, the gel spheres prepared with various values of C had the same percentage of solids, as measured gravimetrically. Thus, the gel spheres presumably have not lost any solids through diffusion, and have the same solids content as the preparation mixture.

All materials were used as supplied, without further purification.

Measurement of swelling

The swelling ratio is defined as V/V_0, where V_0 is the initial volume of the gel (as prepared) and V is the volume of the gel after it had been allowed to swell to its equilibrium size in distilled water. The bulk gel swelling ratio was determined by first carefully breaking the preparation tubes to remove the gel, then cutting the gels into thin sections, and measuring the diameter of the cylindrical samples before and after swelling the samples in a large excess of water for 4 days. The swelling ratio of the gel spheres was determined by measuring the diameter of the spheres, with a low-power microscope, both before and after swelling the samples in water for 2 days. For both the bulk and spherical gels, equilibrium swelling was reached, and the swelling ratio was calculated as $(D/D_0)^3$, where D_0 and D are the initial and swollen diameters respectively.

Measurement of elastic modulus

The elastic modulus of the bulk gels was determined by uniaxial compression measurements performed on an Instron Testing Machine. The gel samples were removed from the preparation tubes, and cut into approximately 1 cm pieces. The diameter and length were measured with callipers. The cylindrical gels were compressed at a rate of 0.508 or 1.27 cm min^{-1} immediately after immersion in water, and before appreciable swelling had taken place.

The elastic modulus of the gel spheres was determined by compressing the spheres between two parallel Teflon plates. The vertical compression and horizontal expansion were determined by viewing the compressed sphere through a low-power microscope, and the force applied was simultaneously determined using an analytical balance. The spheres were immersed in xylene while the measurements were made. The spheres were not immersed in water, as the bulk gels were, because the spheres swelled much more rapidly, and the measured moduli would be affected by this swelling.

EXPERIMENTAL RESULTS

Particle size distribution of gel spheres

Particle sizes were determined by recording the diameters of a sample of 60 to 100 particles for a given run. $\langle D^3\rangle$ and σ_V, the sample standard deviation (assuming a Gaussian distribution) of V, were determined; D is the diameter and V is the volume of a given gel sphere. The average particle diameter and its standard deviation were determined using $D_{av}=\langle D^3\rangle^{1/3}$ and $\sigma_{D_{av}}=2\sigma_V/(\pi\langle D^3\rangle^{2/3})$ respectively. The results for a representative series of runs, using various aqueous phase flow rates, a fixed needle amplitude of 0.90 mm and an 18 gauge, square-tipped syringe needle, are reported in *Figure 2*, where the error bars correspond to $\pm\sigma_{D_{av}}$. The average particle size ranged from 0.33 ± 0.06 to 0.99 ± 0.41 mm for aqueous phase flow rates of 0.78 and 6.45 g min^{-1} respectively.

As is apparent from the figure, for a given set of operating conditions there is significant variability in the particle sizes. Also, it can be seen that the average particle size increases and the particle size uniformity appears to decrease as the aqueous phase flow rate is increased.

Equilibrium swelling

Figures 3 and *4* are representative of the results of swelling of the bulk gels. *Figure 3* is a plot of the swelling ratio *versus* the ageing period for bulk gels prepared without TEMED. The ageing period is defined as the time between the time of sample preparation and the time at which the gels were first immersed in water. It appears that ageing had a relatively small effect on the swelling

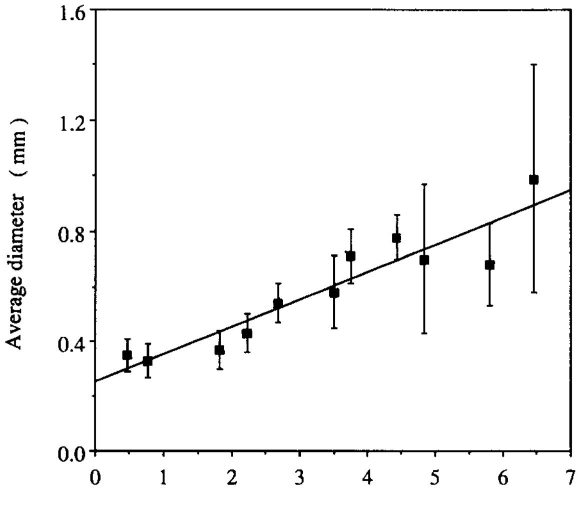

Figure 2 Average gel sphere diameter *versus* aqueous phase flow rate. Operating conditions: 18 gauge, square-tipped needle with an amplitude of 0.90 mm

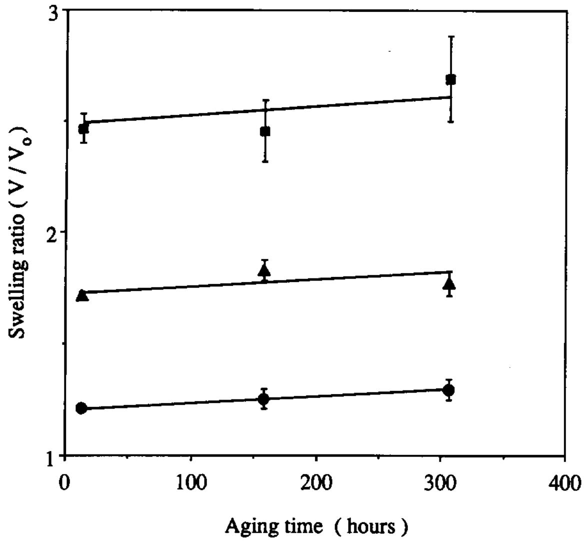

Figure 3 Swelling ratio of bulk gels prepared without TEMED *versus* ageing time: ■, $C = 1.33\%$; ▲, $C = 2.66\%$; *and* ●, $C = 5.32\%$, where C is the weight ratio of crosslinker to monomer

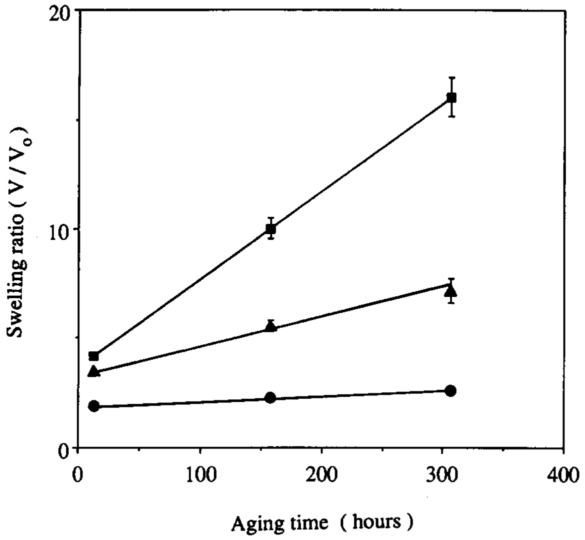

Figure 4 Swelling ratio of bulk gels prepared with 0.11 M TEMED *versus* ageing time. Symbols are as defined in *Figure 3*

ratio of these gels. These results agree reasonably well with those of previous workers[1]. *Figure 4* gives the results of swelling of gels prepared under similar conditions, except that the gels were prepared from solutions containing TEMED at a concentration of 0.11 M. It is apparent that the TEMED had a large effect on the swelling ratio. For the slightly aged gels, there is a small, but significant, increase in swelling, which is seen by comparing the swelling ratio at the lowest ageing period in *Figures 3* and *4*. As the gels age, the effect of the TEMED concentration on the swelling ratio becomes more pronounced, especially in the less highly crosslinked samples. This effect of ageing on the swelling of polyacrylamide gels has been well documented, and has been attributed to hydrolysis[17] and structural changes in these heterogeneous gels[18]. Points along the chain become ionized, and these points repel one another, leading to greater swelling than in the unhydrolysed gel. The presence of TEMED increases the extent of hydrolysis, as it makes the solution more basic.

In *Figure 5*, the swelling ratio of the gel spheres is reported. Each point represents an average of several gel particles, and the error bars denote $\pm\sigma$, where σ is the sample standard deviation for a given ageing time. As with the bulk gels prepared with TEMED, the swelling ratio increased greatly with ageing time, and the increase is largest in the less highly crosslinked samples. Thus, a significant amount of TEMED, which was initially present only in the organic phase, must have diffused into the gel spheres. This could have occurred during the polymerization when the droplet was liquid and also possibly after the droplet had gelled.

Elastic modulus

The elastic modulus of the bulk gels and of the spheres was determined. The modulus of the cylindrical, bulk gels was obtained from the slope of a plot of $-F/A_0$ *versus* $\alpha^{-2} - \alpha$, where $-F$ is the applied force, A_0 is the original cylinder area and $\alpha = L/L_0$ is the compression ratio, with L_0 being the original length and L being the length after compression[19]. A representative plot is given in *Figure 6*, which gives the modulus of $C = 2.66\%$ gels prepared with various amounts of TEMED.

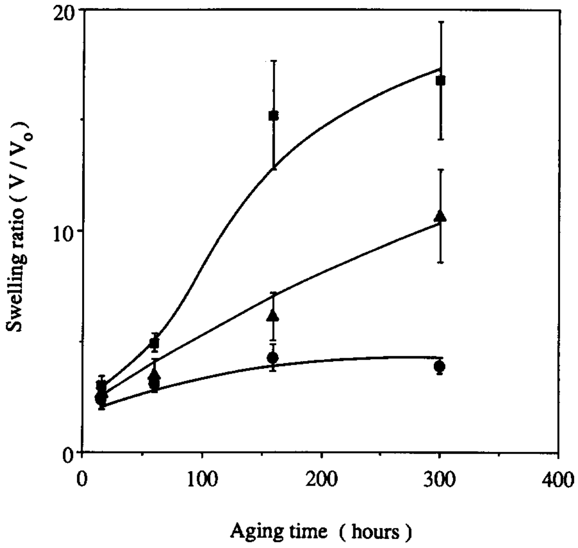

Figure 5 Swelling ratio of gel spheres *versus* ageing time. Symbols are defined as in *Figure 3*

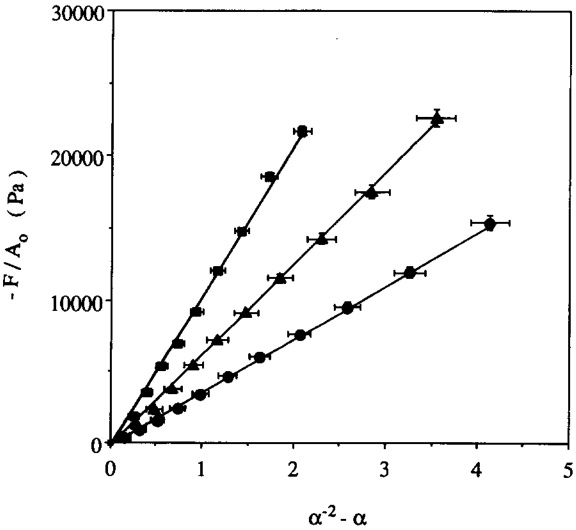

Figure 6 Representative plot for calculating the modulus of bulk gels: $-F/A_0$ *versus* $\alpha^{-2} - \alpha$ for $C = 2.66\%$. Gels prepared with: ■, 0 M TEMED; ▲, 0.11 M TEMED; and ●, 0.26 M TEMED. The moduli of the individual samples are equal to the slopes of the lines

The elastic modulus of the gel spheres was also determined assuming ideal rubber elasticity and a completely homogeneous gel. The spheres were compressed between parallel plates as shown in *Figure 7*, and both the force applied and the change in equatorial diameter were simultaneously measured.

When a force F is applied to an ideal rubber sphere of initial radius R_0 by compressing it between two parallel plates, the stress on a thin slab at the equator (see *Figure 8*) is given by:

$$F/(\pi R_0^2) = NRT(\alpha - \alpha^{-2}) \qquad (1)$$

where F is negative in compression, N is the number of effective elastic chains per unit volume, and $\alpha = \Delta y/\Delta y_0$, where Δy and Δy_0 are the thickness of the stressed and unstressed slabs respectively.

For constant-volume deformation:

$$\pi R_0^2 \Delta y_0 = \pi R^2 \Delta y \qquad (2)$$

where R is the radius of the slab (parallel to the plates) under compression. Thus α can be expressed in terms of the horizontal expansion instead of the vertical compression:

$$\alpha = \Delta y/\Delta y_0 = (D_0/D_h)^2 \qquad (3)$$

where D_h and D_0 are the diameters (measured at the equator) of the stressed and unstressed sphere (see *Figure 7*). Then (1) becomes:

$$-F/(\pi R_0^2) = NRT[(D_h/D_0)^4 - (D_0/D_h)^2] \qquad (4)$$

and the slope of a plot of $-F/(\pi R_0^2)$ *versus* $[(D_h/D_0)^4 - (D_0/D_h)^2]$ gives NRT, the modulus of the sphere.

A representative plot is given in *Figure 9*, for spheres prepared with various amounts of crosslinker. A relation between D_h and D_v, the vertical (compressed) diameter, can be derived[20]. Thus, in principle, instead of measuring D_h, D_v can be measured and converted to D_h, which can be used with (4) to calculate the modulus of the sphere. D_h was measured instead of D_v in this study because limitations in the optics of the apparatus resulted in less reliable values of D_v. To measure D_h, only the 'equator' of the gel must be in sharp focus (see *Figure 7*). This measurement can easily be made whether or not the plates and the sphere are simultaneously in focus. To measure D_v, the 'poles' of the gel must be in sharp focus. This measurement was more difficult to obtain because the poles make physical contact with the plates, which were not in focus when the sphere was, and thus the plates tended to make the image of the poles less distinct, leading to a less accurate determination of D_v compared to D_h.

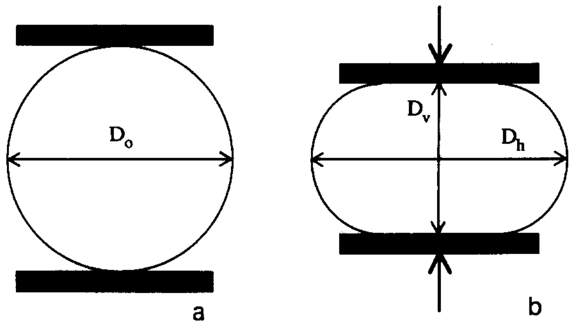

Figure 7 Geometry and notation used for the compression of gel spheres: (a) unstressed sphere and (b) sphere compressed with stress $-F/A_0$, where A_0 is the initial cross-sectional area

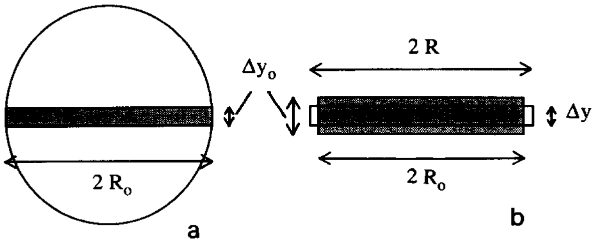

Figure 8 Notation for compression of spheres. The shaded region in (a) is a thin slab at the equator, and is enlarged in (b), where it is shown unstressed (shaded) and compressed (unshaded)

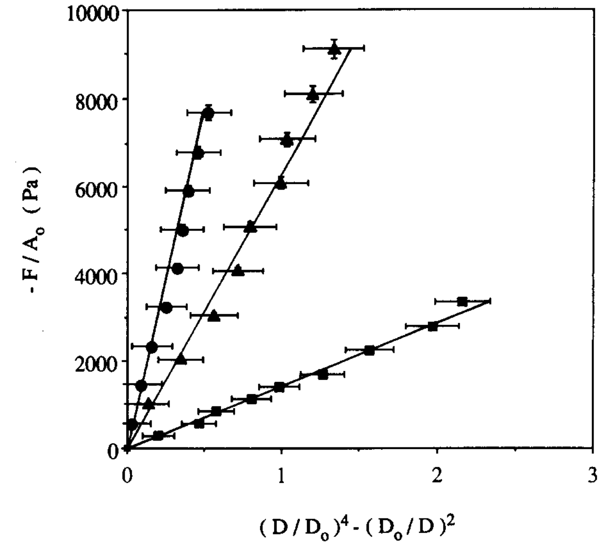

Figure 9 Representative plot for calculating the modulus of gel spheres: $-F/A_0$ *versus* $(D_h/D_0)^4 - (D_0/D_h)^2$ for ■, $C = 1.33\%$; ▲, $C = 2.66\%$; and ●, $C = 5.32\%$

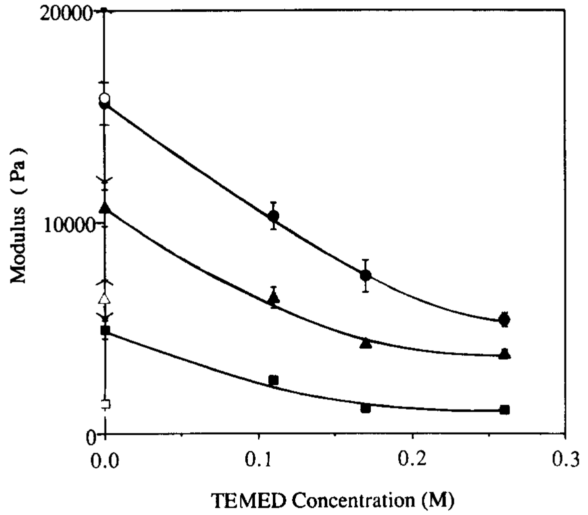

Figure 10 Modulus of bulk gel *versus* TEMED concentration of the preparation mixture for ■, $C = 1.33\%$; ▲, $C = 2.66\%$; and ●, $C = 5.32\%$ gels. The moduli of the gel spheres are indicated on the abscissa for □, $C = 1.33\%$; △, $C = 2.66\%$; and ○, $C = 5.32\%$ gel spheres. The error bars for the gel spheres are denoted with arrows

The modulus of the bulk gels, as determined from plots such as *Figure 6*, *versus* TEMED concentration is given in *Figure 10*. As is apparent from the figure, the modulus is highly dependent upon the TEMED concentration. On the other hand, the modulus did not appear to depend upon the ageing period, which agrees with the reports of previous workers[3,5].

As can be seen from *Figure 10*, the modulus of the bulk gels without TEMED exhibit previously reported behaviour[2,6] of approximate proportionality of modulus to crosslinker concentration at low C and a levelling off as C approaches 5%. The modulus of the spheres is indicated on the abscissa of *Figure 10*. At low C, the modulus is much smaller than the modulus of the corresponding bulk gels and increases much more rapidly with C.

DISCUSSION

The most plausible explanation for the unexpected sphere modulus results is a variation in TEMED concentration. The TEMED concentration is precisely known in the bulk gels. When the gel spheres are prepared, the TEMED concentration of the organic phase is known, but the concentration within the gelling droplet is not. TEMED diffusion into the gelling droplet is expected to slow as the droplet gels. Since the gelation time increases as C decreases, it is plausible that the TEMED concentration in the gel spheres increases with a decrease in C.

From the modulus measurements, the apparent concentration of crosslinks, N_{app}, can be taken as $G/2RT$, where G is the modulus. The results for both bulk gels and gel spheres are reported in *Table 1*, along with N_{stoich}, the stoichiometrically added concentration of crosslinker. N_{app} is observed to be less than N_{stoich} for all of the gels. N_{app} for bulk gels prepared without TEMED is approximately 9–11% of N_{stoich}, which is consistent with previous results[3,6]. There is good agreement between N_{app} for the bulk gels and gel spheres when $C=5.32\%$. As C is reduced, deviations occur. By postulating that the TEMED concentration in the spheres is the same as the TEMED concentration in bulk gels with the same N_{app} (or modulus), one obtains that the TEMED concentrations are 0–0.06 M, 0.07–0.12 M and 0.14–0.20 M for gel spheres with $C=5.32\%$, 2.66% and 1.33% respectively. The range in concentrations of TEMED is a consequence of the uncertainty in $\mathrm{N_{app}}$.

It should be noted that it appears that the marked increase in N_{app} of the gel spheres when C is increased from 1.33% to 2.66% and the smaller increase in N_{app} when C is increased to 5.32% appears similar to the behaviour of N_{app} for the high-TEMED-concentration bulk gels (see *Figure 10*). However, it would be incorrect to conclude that all of the gel spheres have high TEMED concentrations since N_{app} for the $C=5.32\%$ gel spheres is considerably greater than that of the high-TEMED-concentration bulk gels of the same crosslinker concentration.

Swelling measurements are often used to estimate the number of effective elastic chains. However, with swelling ratios that are strongly dependent on ageing due to the presence of TEMED, such estimates from swelling results would not lead to any greater insight than was previously obtained by examining the swelling ratios themselves. Since N_{app} from the modulus measurements is age-independent, it gives a more reliable estimate of the effective crosslinker concentration.

We also considered the possibility that the crosslink density of the gel spheres is not uniform, but is lower at the core than in the shell. If so, the plots used to predict the modulus, such as *Figure 9*, will not give the true modulus, since they assume a uniform modulus throughout the particle. Also, N_{app} from modulus results would not be correct, since the predictions assume an isotropic network. Such a possibility would lead to a size-dependent modulus. Within experimental error, no size dependence was observed for the modulus of spheres ranging from 0.3 to 0.85 mm in diameter. However, small differences in the modulus of a gel sphere could not be determined with the available apparatus, as is readily apparent from the size of the error bars in *Figure 9*.

CONCLUSIONS

Polyacrylamide gel spheres were prepared using a suspension polymerization technique, with TEMED, an initiator, in the continuous phase. Larger, 'bulk' gels were prepared under similar conditions. Equilibrium swelling in water and the elastic modulus were determined for various crosslinker concentrations for both the gel spheres and the bulk gels. Equilibrium swelling of the gel spheres was highly age-dependent, and by comparison with the swelling of bulk gels, a significant amount of TEMED diffusion into the gel spheres was inferred. Elastic modulus measurements were used to determine the apparent crosslink density, N_{app}. There was good agreement between N_{app} for the gel spheres and the bulk gels at high C, but deviations occurred at lower C. These results can be explained by assuming that more TEMED diffused into the low-C spheres than the high-C spheres, a plausible assumption, since the low-C spheres are expected to have a longer gelation time.

The method of production of spherical gel particles presented here could be improved upon in a number of ways. The use of a longer column could eliminate the need for stirring, as the particles could settle slowly, and be completely polymerized by the time they reached the bottom of a sufficiently long column. This would further reduce droplet coalescence, and lead to a more uniform size. Also, the top of the existing vessel was open to the atmosphere during the aqueous phase introduction step. This inevitably introduces oxygen into the system and lengthens the induction period. If this could be minimized, less or no TEMED could be used and less hydrolysis would result.

Table 1 N_{app} from elastic modulus for gel spheres and bulk gels with various TEMED concentrations

		$N_{\mathrm{app}}\times 10^{-18}$ (cm^{-3})				
			Bulk gels: TEMED concentration (M)			
C (%)	$N_{\mathrm{stoich}}\times 10^{-18}$ (cm^{-3})	Gel spheres	0	0.11	0.17	0.26
5.32	20.8	1.96±0.50	1.92±0.12	1.26±0.10	0.91±0.09	0.66±0.04
2.66	10.4	0.78±0.11	1.31±0.10	0.79±0.06	0.51±0.01	0.46±0.03
1.33	5.20	0.18±0.03	0.60±0.06	0.31±0.01	0.14±0.01	0.14±0.01

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