Shear modulus of polyelectrolyte gels under electric field

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Abstract

The shear modulus of two polyelectrolyte gels poly(acrylic acid), a weak acid with small side groups, and poly(2-acrylamide-2- methylpropane sulfonic acid), a strong acid with large side groups, have been measured with and without application of an electric field across a gel sample swollen with water to equilibrium. In the absence of electric field the shear modulus of PAMPS gels made to different crosslink degrees is shown to be inversely proportional to the swelling degree, in accord with theoretical prediction. Under a steady electric field the measured modulus of these gels is seen to reduce with time. This is explained by migration of the free counter ions and associated water towards the cathode, resulting in reduced contact between gel and rheometer due to exuded water. Theoretical prediction of G' and G'' in the presence of a thin slip layer are in good quantitative agreement with experimental observation. Preliminary measurements of the reduction of shear modulus under pulsed electric field have been obtained and an unexpected recovery of the initial modulus is seen on all subsequent applications of the field, before the continued reduction to successively lower values. When roughened platens are used a step-wise variation in measured modulus is seen, with a slightly lower modulus being recorded in the presence of an applied electric field.

(Some figures in this article are in colour only in the electronic version; see `www.iop.org`)

1. Introduction

Polyelectrolyte gels are molecular networks (often chemically cross-linked) made from monomers that contain ionizable groups and swollen with a solvent (usually water). These gels exhibit reversible swelling and contraction (often by a factor of greater than 100) under various stimuli such as change of pH, temperature and electric field. The swelling degree of such gels has been widely studied as a function of degree of ionization of the polymer chains, crosslink degree of the network, concentration of salt added and composition of the solvent [1–9].

The shear modulus of charged gel networks has been seen to decrease as the charge concentration on the polymer chain is increased [8,10–14]. Skouri *et al* [12] have also shown

that addition of salt to screen the electrostatic interactions allows the modulus of the un-ionized gel to be recovered.

Electric field induced deformation of polyelectrolyte gels was first reported by Hamlen *et al* in 1965 [15] and since then research in this area has continued steadily, but with recent renewed vigour. Depending on the geometry of the gel, and its proximity to the electrodes, shrinking and bending effects are seen under electric field. A strip of gel placed with its long axis parallel to (but not touching) the electrodes, will bend like a bi-metal [16–20], however, gels placed with their long dimension spanning the gap between the electrodes are seen to shrink preferentially at one end [17,21]. Osada has also reported water dripping out of the gel at the cathode [18,19]. This deformation has been explained as due partly to a change in the osmotic pressure caused by the difference in free ion concentration inside and outside the gel, and partly to decreasing polyion concentration, due to electrolysis [22].

As a result of this research polyelectrolyte gels have been proposed for applications in smart devices such as sensors, large motion actuators, controlled drug release, membrane separation, super absorbents and artificial muscles [16,23–26]. In view of the fact that electric field is such a conventional and practical method of actuation, there is a pressing need to determine quantitative mechanical properties for the different classes of polyelectrolyte gel under electric field. This paper examines the change in the measured mechanical properties of polyelectrolyte gels in response to an applied electric field, and reports a novel effect.

2. Experimental details

2.1. Preparation of gels

Two differing gel systems were investigated. The first of these was the weakly ionizing poly(acrylic acid) (PAA) which has a small side group containing the ionizable moiety (figure 1). The second was poly(2-acrylamide-2-methylpropane sulfonic acid) (PAMPS), (figure 1) which is a strong acid with side groups much longer than the monomeric repeat distance along the chain backbone. The charged sites reside at the ends of these side groups.

Gels were prepared by the well established method of free radical polymerization [11,12,19,21,27–30]. Crosslink degree (r_c, defined as the molar fraction of crosslinker to total monomer content) was varied by inclusion of N,N-methylene bis(acrylamide) (BIS). Potassium persulfate (PP) was used as an initiator. All chemicals were purchased from Aldrich. The crosslinker and initiator were mixed with distilled deionized water and heated to around 30 °C while being stirred magnetically. The monomer was then added and heating continued. Stirring was ceased at about 40 °C and the mould (described below) was lowered into the solution. Gelation occurred between 60 °C and 80 °C for PAA and between 50 °C and 70 °C for PAMPS.

To produce flat parallel-sided samples a mould was used consisting of two flat glass plates (100 mm×100 mm×2 mm) maintained at fixed separation by 1.5 mm or 3 mm glass spacers and fastened by two Supaclips™ (as shown in figure 2). Gels were allowed to cool to below 60 °C (for ease of handling) before being removed by carefully peeling the mould apart. The gel was cut into sections and washed (to remove the initiator and any un-reacted monomers) by placing it into a large excess of distilled deionized water, which was refreshed every day for two weeks. The degree of ionization was varied by swelling the PAA gels in solutions of sodium hydroxide, made to different molarities, and by co-polymerization of the AMPS monomer with the non-ionizable monomer N,N-dimethyl acrylamide (DMAA) in various molar ratios (see tables 1 and 2).
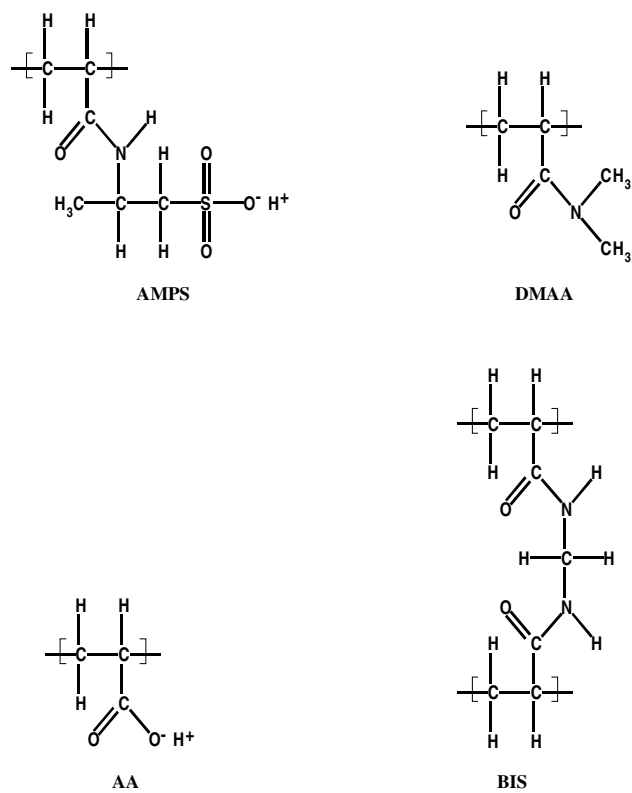
Figure 1. Monomers used to make gels. AMPS = 2-acrylamide-2-methylpropane sulfonic acid; DMAA = N,N-dimethyl acrylamide; AA = acrylic acid; BIS = N,N-methylene bis(acrylamide).
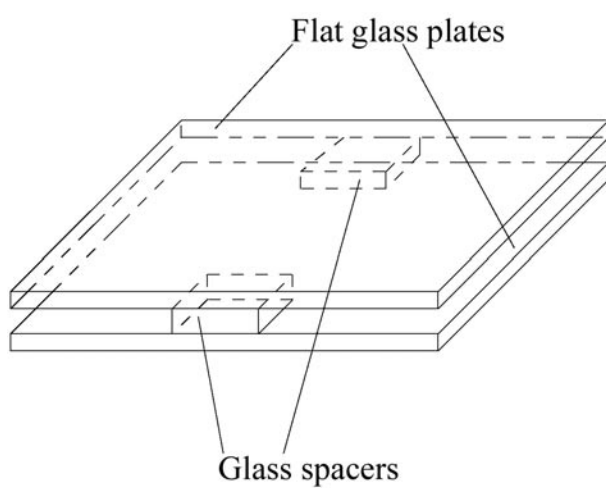
Figure 2. Glass mould used to produce parallel-sided gel samples.

Table 1. Details of PAA gels.

Sample code	Moles at synthesis				r_c	N	C_0 (M)	C_{eq} (M)	f	G' (Pa)	Q
	AA	BIS	PP	H$_2$O							
a3r06	2.036	0.013	0.011	22.543	0.0065	77	3.69		0	3.0×10^4	
a4r08	0.496	0.004	0.004	10.075	0.0079	63	2.29		0		
a4ir08	0.549	0.005	0.006	10.699	0.0082	61	2.38		0		
a1ir13	0.498	0.006	0.008	9.434	0.0129	39	2.44		0	3.9×10^4	
a5ir20	0.520	0.011	0.006	2.080	0.0202	25	6.93		0	4.4×10^4	
a2ir25	0.554	0.014	0.007	9.573	0.0247	20	2.65		0	7.1×10^4	
a3ir42	0.491	0.021	0.006	10.139	0.0419	12	2.32		0	7.8×10^4	
a2r06f000m	1.104	0.007	0.004	9.339	0.0060	83	4.46	2.24	0		12
a2r06f025m	1.104	0.007	0.004	9.339	0.0060	83	4.46		0.25		
a2r06f050m	1.104	0.007	0.004	9.339	0.0060	83	4.46	0.98	0.50		20
a2r06f100m	1.104	0.007	0.004	9.339	0.0060	83	4.46	1.07	1		23
a2r06f200m	1.104	0.007	0.004	9.339	0.0060	83	4.46	3.00	2		14
a2r06f400m	1.104	0.007	0.004	9.339	0.0060	83	4.46	6.13	4		12
a1r13f000m	1.042	0.014	0.005	11.971	0.0133	38	3.61	1.15	0		7
a1r13f025m	1.042	0.014	0.005	11.971	0.0133	38	3.61	0.85	0.25		28
a1r13f050m	1.042	0.014	0.005	11.971	0.0133	38	3.61	1.52	0.50		13
a1r13f100m	1.042	0.014	0.005	11.971	0.0133	38	3.61	2.05	1		12
a1r13f200m	1.042	0.014	0.005	11.971	0.0133	38	3.61	1.98	2		9
a1r13f400m	1.042	0.014	0.005	11.971	0.0133	38	3.61	2.76	4		7

AA = acrylic acid.
BIS = N,N-methylene bis(acrylamide).
PP = potassium persulfate.
For PAA gels r_c = moles of AA/moles of (AA+BIS).
N = monomer units per strand between crosslink points = $1/(2r_c)$.
C_0 = polymer concentration at synthesis (monomer moles per litre).
C_{eq} = polymer concentration at swelling equilibrium (monomer moles per litre).
f = molarity of sodium hydroxide solution used to swell gels.
Q = swelling degree = mass when swollen to equilibrium/mass when dried (compensating for NaOH contained within dried gel).
G' = storage shear modulus (Pa).

2.2. Dynamic mechanical analysis

The mechanical properties of the gels were analysed using a modified SR500 stress-controlled Rheometric Scientific rheometer with 23.5 mm diameter parallel platens in oscillatory mode. To apply an electric field to the gel the terminals of a stabilized DC power supply were connected to the platens of the rheometer by soldering fine wires to the outer surface of each platen, thus making good electrical contact yet not interfering with the measurement of gel modulus. Voltages of $\sim$3 V were applied over gel thicknesses of approximately 3 mm, the bottom platen having a positive potential with respect to the earthed upper platen.

Before mounting in the rheometer the gels were cut into 23.5 mm diameter discs using a sharpened cylindrical cutter, and placed on a paper towel to remove excess water from all surfaces. Once in the rheometer the gels were compressed to 0.75 of their thickness at equilibrium swelling to ensure good mechanical contact with the platens. To improve contact between gel and platens still further, some experiments were carried out using roughened platens, which had raised square studs over their surface (each stud was 2 mm across and 1 mm in depth). All measurements were taken at a frequency of 1 rad s^{-1} with a stress amplitude of 100 Pa.

Table 2. Details of PAMPS gels.

Sample code	Moles at synthesis					r_c	N	C_0 (M)	C_{eq} (M)	f	G' (Pa)	Q
	AMPS	DMAA	BIS	PP	H_2O							
p03r11f99	0.180	0.000	0.002	0.002	5.749	0.011	47	1.29	0.02	100	4.0×10^3	304
p01r19f99	0.178	0.000	0.004	0.002	5.573	0.019	26	1.32	0.02	100	1.2×10^4	276
p02r29f99	0.184	0.000	0.005	0.002	6.180	0.029	17	1.26	0.08	100	4.9×10^4	58
p05r34f99	0.179	0.000	0.006	0.003	5.996	0.034	15	1.27	0.09	100	4.3×10^4	52
p07r51f99	0.241	0.000	0.013	0.003	9.404	0.051	10	1.15	0.23	100	1.4×10^5	21
p06r54f99	0.182	0.000	0.010	0.004	5.604	0.054	9	1.37	0.23	100	1.6×10^5	21
pr19f51	0.144	0.137	0.005	0.005	7.003	0.019	26	1.68	0.38	51		17
pr23f00	0.000	0.874	0.021	0.007	16.921	0.0234	21	2.27	3.66	0		6

AMPS = 2-acrylamide-2-methylpropane sulfonic acid.
DMAA = N,N-dimethyl acrylamide.
BIS = N,N-methylene bis(acrylamide).
PP = potassium persulfate.
For PAMPS gels r_c = moles of AMPS/moles of (AMPS+DMAA+BIS).
N = monomer units per strand between crosslink points = $1/(2r_c)$.
C_0 = polymer concentration at synthesis (monomer moles per litre).
C_{eq} = polymer concentration at swelling equilibrium (monomer moles per litre).
f = degree of ionization (molar % of AMPS monomer).
Q = swelling degree = mass when swollen to equilibrium/mass when dried.
G' = storage shear modulus (Pa).

2.3. Rate of water evaporation

To determine the amount of water lost by a gel due to evaporation whilst in the rheometer, a gel disc was mounted between two platens and placed on a sensitive top-pan balance. The weight of the gel was recorded at intervals for over four hours.

2.4. Swelling degree

The swelling degree (Q) was determined by weighing a fully swollen piece of gel and then allowing it to dry in the laboratory for two weeks. The gels were then placed in a vacuum oven at about 100 °C overnight, allowed to cool to room temperature in a dessicator and then re-weighed. This drying procedure was repeated until the mass determined was constant to within $\pm5 \times 10^{-5}$ g, which was usually the case after a single exposure to the vacuum oven. The swelling degree was then determined as the ratio of mass when fully swollen to mass when completely dried, with a correction being made for PAA gels to account for the NaOH contained within the dry gel.

3. Results and discussion

3.1. Swelling equilibrium, shear modulus, crosslink degree and charge density

For PAMPS gels the swelling degree increases rapidly with increasing linear charge density (figure 3). This is in qualitative agreement with published work [31] and is explained as due to the increased osmotic pressure from the increased number of free counter ions. For PAA gels over the range of sodium hydroxide molarities used, it can be seen that the swelling degree rises rapidly to a maximum before tailing off (figure 4). This suggests that at molarities greater than about 0.25 M the sodium hydroxide is not only promoting ionization of the PAA chain, but
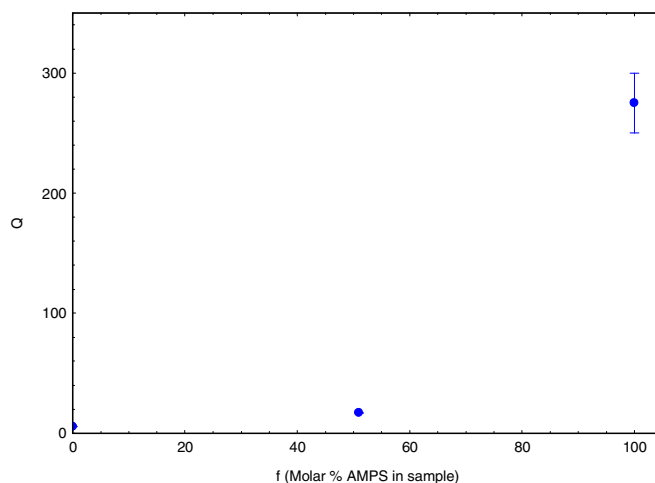
Figure 3. Swelling degree with molar % of ionizable monomer AMPS, for PAMPS gels with $r_c = 0.02$.
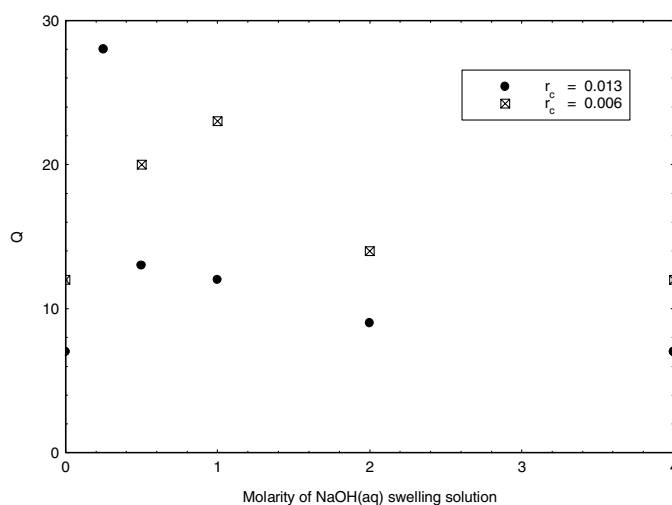

Figure 4. Swelling degree with molarity of sodium hydroxide solution used to ionize PAA gels.

is supplying sufficient free ions to screen the electrostatic interactions of the polymer chains, and hence to reduce the swelling degree.

The factor of approximately 10 between the maximum swelling degree of PAMPS and PAA gels can be accounted for by several reasons. Firstly, only discrete molarities of NaOH were used to neutralize the PAA gels, with the result that the true peak swelling may not have been observed. Secondly, even at this peak swelling the PAA may not be fully ionized. However, in reality it is probably the screening effect of the free ions that has the largest effect, since allowing a fully swollen PAMPS gel to equilibrate in 0.25 M NaCl solution reduced its swelling degree by a factor of four.
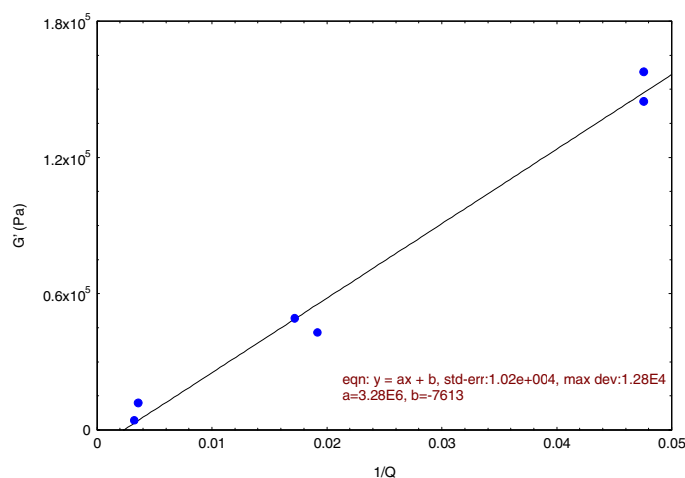
Figure 5. Storage shear modulus with reciprocal swelling degree for a range of PAMPS gels.
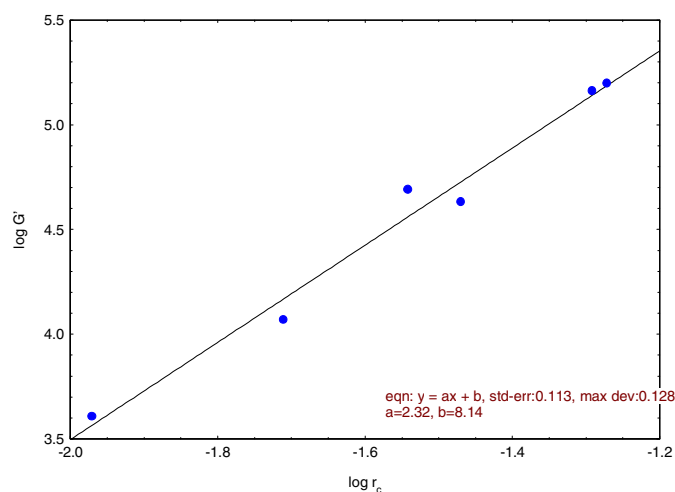

Figure 6. Storage shear modulus with crosslink degree for PAMPS gels swollen to equilibrium.

The shear modulus for PAMPS gels can be seen in figures 5 and 6. The data in figure 5 are in agreement with the prediction by Rubinstein *et al* [5] that the modulus at swelling equilibrium is inversely proportional to the swelling degree (providing the linear charge density remains constant). Figure 6 shows the shear modulus increasing with crosslink degree, as expected, since even at fixed polymer concentration gels with higher crosslink degree would have a higher modulus due to a higher density of network strands. In addition to this gels with higher crosslink degree have lower swelling degrees and this enhances the rise of modulus with crosslink degree.

Before investigating the mechanical properties of these gels under electric field, it was first necessary to determine the amount of water lost from a gel over time under static conditions when sandwiched between the rheometer platens. A PAMPS gel was found to
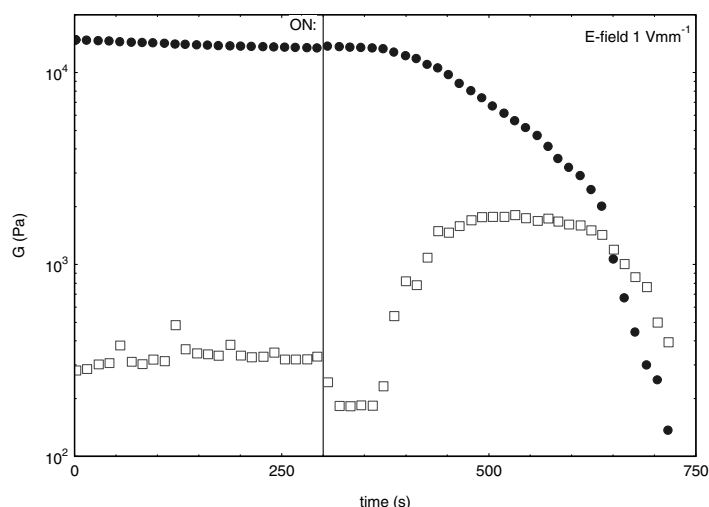
Figure 7. Measured storage (●) and loss (□) moduli for PAMPS gel using smooth platens with steady electric field applied across gel at time = 300 s.

lose approximately 5% mass per hour. However, on the timescale of a rheological experiment (say 20 minutes) the water lost by evaporation would be typically <2%.

As a further control experiment the moduli of a PAMPS gel were repeatedly measured over time with zero electric field applied. The loss modulus remained constant but the storage modulus fell steadily by a factor of two over an hour. This drop in storage modulus could be explained by the loss of water by evaporation if either (1) the gel disc was losing contact with the platens at the edges, due to contraction on drying out, or (2) the gel network was so swollen that the chains were extended well beyond the gaussian limit, resulting in a reduction of modulus with reduction in volume.

3.2. Dynamic mechanical properties under electric field

3.2.1. Steady field The mechanical response of PAMPS gels under steady electric field (typically ~ 1 V mm^{-1}) can be seen in figure 7. The reduction in G' can be explained by the formation of a thin layer of water between the gel and the rheometer platen resulting from the transport of water dragged by the free counter ions as they migrate towards the cathode under the influence of the electric field. Such exudation of water has previously been reported in the literature [18,19]. Theoretical prediction of the variation of G' and G'' with thickness of 'slip layer' is given in the appendix, and predicted values are in good quantitative agreement with experimental observation.

3.2.2. Pulsed field When the electric field is applied to the gel in a pulsed manner (typically on for 30 ± 5 s and off for 200–300 s) an unexpected phenomenon is observed (see figure 8). Using smooth platens G' is reduced (as expected) as a result of the first field pulse. Note that if the pulse is short the reduction in G' is only seen after the field has been switched off, presumably due to the finite time needed for the agitation of the rheometer to allow the exuded water to spread evenly over the surface of the gel. The unexpected phenomenon is that on subsequent applications of the field G' shows an immediate rise of more than an order of magnitude to recover its initial value, (and then subsequently falls to a lower value than
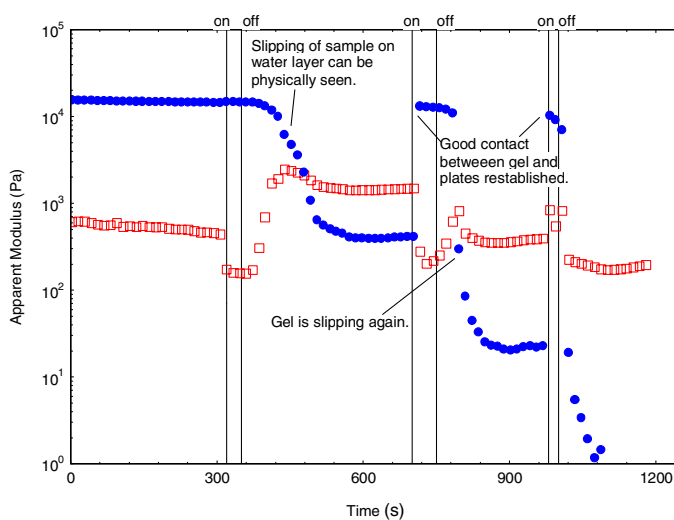
Figure 8. Measured storage (●) and loss (□) moduli for PAMPS gel ($r_c = 0.02$) using smooth platens with electric field pulses as shown.

after the previous application of the field). After a few applications of the field G' does not recover its initial value when the electric field is switched on, and it is assumed that so much water has been exuded from the gel that contact is lost between gel and rheometer. To aid understanding, other tests were carried out where the direction of the field was reversed for the second application of the field, but rapid recovery of G' was still seen.

A similar effect was observed with PAA gels (figure 9) although to a much lesser degree, presumably due to the significantly lower degree of ionization and hence lower concentration of free counter ions causing much less water to be transported and exuded from the gel.
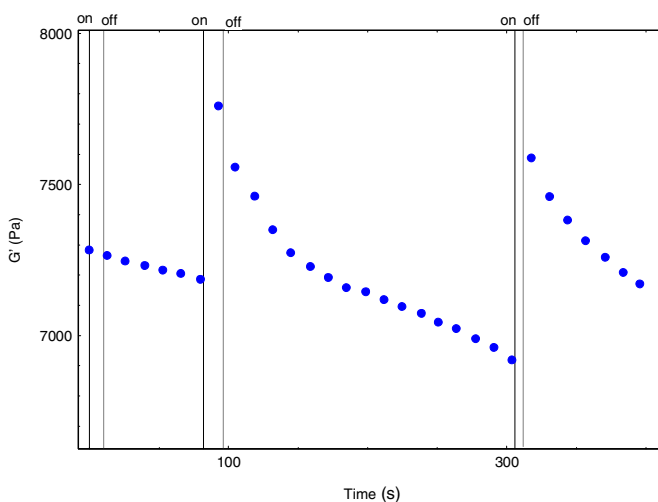

Figure 9. Measured storage (●) modulus for PAA gel ($r_c = 0.02$) using smooth platens, with electric field pulses as shown.

Field pulses of one second duration (or even less) are still sufficient to cause contact to be briefly regained between the gel and the platens, and G' to return momentarily to its original value. If the time *between* two pulses is too short, then the gel behaves as if there was only one long pulse. Short, in this, case relates to the time it takes for the measured gel modulus to stabilize after G' has started to reduce (typically 100 s). The experiments are most repeatable if the gel is allowed to stabilize between each application of the field.

3.2.3. Rough platens With rough platens (having raised square studs 2 mm across and 1 mm in depth covering the surface) both PAMPS and PAA gels show different behaviour from that with smooth platens. Now G' is reduced on application of the field and restored on removal of the field in a step-wise manner (see figures 10 and 11), the magnitude of this change being significantly smaller than with smooth platens for the PAMPS gels. However the dramatic recovery of G' on application of the field can sometimes be observed with rough platens for PAMPS gels, presumably when a significant amount of water has been exuded.
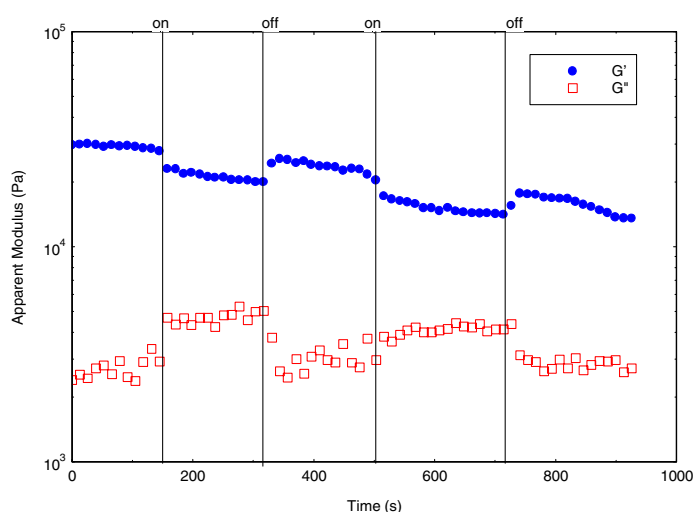

Figure 10. Measured storage and loss shear moduli for PAMPS gel ($r_c = 0.02$) using rough platens, with electric field pulses as shown.

The observations presented here are of a preliminary nature, and a more rigorous investigation is currently being undertaken. So far all the evidence points towards these effects being due (at least in part) to the transport of free ions and water under the electric field. This is confirmed by experiments on uncharged polypropylene sponge discs which exhibited the step-wise variation of modulus when soaked in salt solution, although they exhibited no variation of modulus when dry, or soaked in distilled deionized water. The transport of ions and water towards the cathode under electric field and their randomization back into the bulk of the gel could possibly explain the behaviour of polyelectrolyte gels with rough platens, but the dramatic recovery of G' on application of the field with smooth platens remains unexplained as yet.

4. Conclusions

The shear modulus of PAA and PAMPS gels has been measured at swelling equilibrium both with and without application of an electric field (~ 1 V mm^{-1}) across the gel. In the absence of
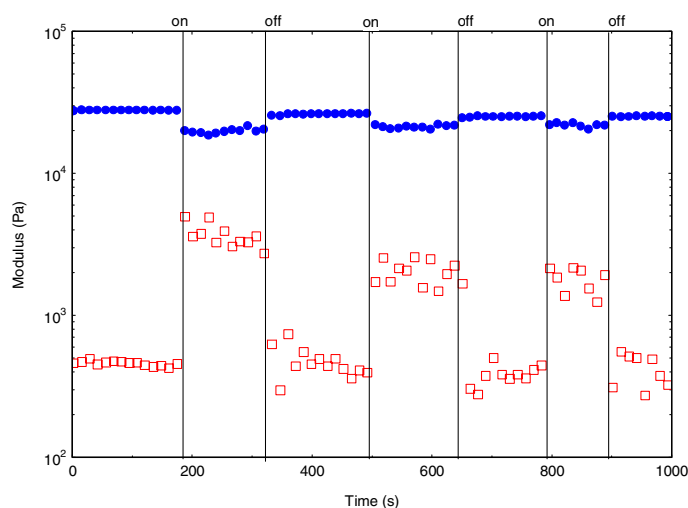
Figure 11. Measured storage (●) and loss (□) moduli for PAA gel ($r_c = 0.02$) using rough platens, with electric field pulses as shown.

electric field the modulus of PAMPS gels made to different crosslink degrees has been shown to be inversely proportional to the swelling degree. This result is in accordance with theoretical predictions by Rubinstein *et al* [5].

Under steady electric field the measured storage modulus of PAMPS gels using smooth platens is reduced with time. This has been attributed to reduced contact between gel and rheometer due to exuded water, forming a slip layer. Theoretical prediction of G' and G'' (see appendix) is in good quantitative agreement with experimental observation, assuming a slip layer which is a few nanometers in thickness.

If the electric field is applied in discrete pulses (on for ~ 30 s and off for ~ 200 s) then on each subsequent application of the field the initial measured storage modulus is recovered briefly before being reduced further. This implies that good contact between gel and rheometer platens is momentarily regained, but the explanation of this novel phenomenon is still under investigation.

When roughened platens are used a different effect on the measured modulus of these gels under electric field is seen. Here the modulus is reduced on application of the field, and recovered on removal of the field, in a step-wise fashion (the magnitude of any change in modulus for PAMPS gels being at least an order of magnitude less than when smooth platens are used). Experiments with polypropylene sponges soaked in salt solution indicate that this effect is predominantly due to the motion of the free ions, and their associated water molecules.

Appendix

To calculate the effective shear modulus for a gel that has a thin layer of water (slip layer) between it and the rheometer platens: The shear stress in the bulk gel is given by

$$\sigma(\omega) = G(\omega)\gamma_{\text{gel}}(\omega) \tag{A.1}$$

where G is the gel shear modulus and γ_{gel} is the local strain in the gel.

Top platen	
Slip layer (η)	↑ ↑ t ↓
	H
Bulk gel (G)	
	↓
Bottom platen	

The shear stress in the slip layer is;

$$\sigma = \eta\dot{\gamma}_{\text{fluid}} \tag{A.2}$$

where η is the viscosity and γ_{fluid} is the local strain in the fluid. The boundary condition is that the shear stress in the fluid and the gel must be equal, so that;

$$i\omega\eta\gamma_{\text{fluid}} = G(\omega)\gamma_{\text{gel}}. \tag{A.3}$$

The apparent measured strain is;

$$\gamma_{\text{app}} = \frac{\gamma_{\text{gel}}(H-t) + \gamma_{\text{fluid}}t}{H} \tag{A.4}$$

where t is the thickness of the slip layer and H is the total thickness. Equation (1) can thus be rewritten in terms of the apparent strain, as;

$$\sigma(\omega) = G_{\text{eff}}(\omega)\gamma_{\text{app}}(\omega). \tag{A.5}$$

The real and imaginary parts can be extracted, according to $G_{\text{eff}} = G'_{\text{eff}} + iG''_{\text{eff}}$ as;

$$G'_{\text{eff}}(w) = \frac{(1-x)\lambda^2 G'_{\text{gel}}(\omega)}{x^2 + (1-x)^2\lambda^2} \tag{A.6}$$

$$G''_{\text{eff}}(\omega) = \frac{x\omega\eta + (1-x)\lambda^2 G''_{\text{gel}}(\omega)}{x^2 + (1-x)^2\lambda^2} \tag{A.7}$$

where

$$x = \frac{t}{H} \qquad \text{and} \qquad \lambda = \frac{\omega\eta}{\left|G_{\text{gel}}\right|}. \tag{A.8}$$

Assuming $x \ll 1$, equations (6) and (7) can be approximated as;

$$G'_{\text{eff}}(w) = \frac{\lambda^2 G'_{\text{gel}}(\omega)}{x^2 + \lambda^2} \tag{A.9}$$

$$G''_{\text{eff}}(\omega) = \frac{x\omega\eta + \lambda^2 G''_{\text{gel}}(\omega)}{x^2 + \lambda^2}. \tag{A.10}$$

From figure 8 the initial values of shear modulus are

$$G'' = 1.5 \times 10^4 \text{ Pa} \qquad G' = 6.0 \times 10^2 \text{ Pa}$$
$$|G_{\text{gel}}| = 1.5 \times 10^4 \text{ Pa} \qquad \omega = 1 \text{ rad s}^{-1} \qquad H = 3 \times 10^{-3} \text{ m}$$

Table A1. Predicted values.

t (m)	10^{-9} m	10^{-8} m
G'_{eff} (Pa)	5.8×10^2	6.0×10^0
G''_{eff} (Pa)	2.9×10^3	3.0×10^2

For water $\eta = 10^{-3}$ Pa s.

This yields predicted values given in table A1.

Comparing these predicted values with the data in figure 8 shows good quantitative agreement. After 600 s, when the moduli have reached a local plateau, their values are consistent with a water layer of the order of a nanometer in thickness. By 1100 s the moduli are consistent with a layer of water 10 nm in thickness.

By the calculation above it has been shown that a slip layer of thickness only one nanometer results in a reduction of G' by about one and a half orders of magnitude, and a rise in G'' by slightly less than an order of magnitude. However, even with this slip layer it is still possible to obtain a reasonable elastic reponse.

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