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A spectroscopic study of polyelectrolyte solutions under shear

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Abstract

The chain segment orientation of the polyelectrolyte poly(styrene sulfonate), PSS, in glycerol solutions under shear have been studied using a novel Ultra Violet rheo-optic technique. The extinction coefficient of the polyelectrolyte in solution, ϵ, was measured using unpolarised light perpendicular to the direction of flow and is shown to decrease upon the application of shear. When the incident light was polarised with the direction of shear the reduced change in extinction coefficient of the polyelectrolyte became more negative with shear. For light polarised perpendicular to the shear direction the reduced change in extinction coefficient of the polyelectrolyte increased, became more positive, with the application of shear. There was no shear-induced change in the reduced change in extinction coefficient of the polyelectrolyte backbone for light polarised at 67° to the direction of shear. All shear-spectroscopic behaviour may be explained by the alignment of the polarised PSS monomer units in the direction of shear. The maximum dichroic ratio for the polyelectrolyte chain is related to the chain polarisability and was predicted from the angular dependence of the change in extinction measurements to be approximately 2.35.

Keywords: Rheo-optic; Poly(styrene sulfonate); Shear

1. Introduction

Polyelectrolytes are polymers containing ionisable groups that can dissociate in polar solvents, such as water, to form a charged polymer. By varying the electrostatic nature of the solution the degree of monomer counter ion dissociation may be controlled [1,2]. In a solution of high salt concentration, the electrostatic repulsion between the charged groups of the polyion is screened and the macromolecule behaves more like a neutral polymer. As the concentration of added electrolyte is reduced the electrostatic repulsion between the ionised monomer units becomes significant and the macromolecule backbone stretches out and adopts a more open conformation. The control of the electrostatic nature of the solvent enables changes in the polyelectrolyte conformation that are reflected in the solutions rheological properties. Due to their large size in solution and shear thinning behaviour at relative low shear rates, polyelectrolytes have many industrially relevant applications as drag reducers and additives to high shear processes. An increased understanding of the behaviour of polyelectrolytes is also of biological importance as many biopolymers, such as DNA, are polyelectrolytes.

Rheo-optic techniques allow for the non-intrusive measurement of a macromolecule solutions microstructure under shear [3,4]. Shear induced anisotropy in the refractive index is attributed to orientation of the optically active components within the solution. The optical anisotropy of poly(styrene sulfonate), PSS, arises from the anisotropy in the monomer units. Due to the paucity of polarisability data on the styrene sulfonate group, its optical properties are assumed to be analogous to the styrene group. For polystyrene the measured polarisability, $\Delta\alpha = \alpha_1 - \alpha_2$, is negative in the direction of the polymer backbone. This is due to the absorption transition dipole of the styrene groups being oriented perpendicular to the main axis of the backbone [5].

In the quiescent state, all molecular orientations are likely, therefore, there is no anisotropy in the material refractive index, n. If the chain segment is aligned in the direction of flow, the material refractive index will depend on relative orientation of the segment to the orientation of the incident light. For a macromolecule under flow, alignment of the optical segments leads to measurable change in the refractive index [6]. The birefringence, $\Delta n'$, for the polystyrene chain under shear is shown to be negative, resulting from the negative stress optic coefficient [7].

Whilst the flow birefringence of neutral polymer systems has been extensively studied, the study of charged polyelectrolytes by flow birefringence is relatively uncommon [8,9]. Zebrowski and Fuller used a polarisation modulation optical

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Table 1
Molecular weight properties for sodium poly(styrene sulfonate)

Measured M_w, (kg mol^{-1})	M_w/M_n
1500	2.2
360	2.5
190	2.7

train to measure the flow-induced birefringence of PSS in electrolyte solutions [8]. Flow birefringence has also been used to test the stress optic law for semi-dilute and concentrated salt free solutions of PSS [10]. The relaxation times for mechanical and birefringence measurements over two decades of concentration were found to correspond well, leading to the prediction of the stress optic coefficient. The observed relaxation behaviour corresponded with the theoretical predictions for a transition from a system of simple Rouse dynamics for an unentangled chain to reptation dynamics for an entangled chain [10,11].

The work by Michl and Thulstrup has described the orientation of various compounds by 'orientation factors', which are dependent on the molecular shape and light attenuation properties of each selected compound [12]. The orientation factors, K_u, may be used to describe the degree of alignment of the molecular axis with the U axis. The origins and further discussion of the orientation factors may be found elsewhere [12]. In the quiescent and aligned cases it is shown that $K_z + K_y + K_x = 1$. For an attenuating compound in the quiescent state the orientation factors, $K_z = K_y = K_x = 1/3$, as all orientations are equally possible. The K_z and K_y values were measured and the value for K_x, which is always less than K_y, is subsequently calculated. The K_z value represents the longest or major (z) axis of the molecule, with both K_y and K_x perpendicular to each other and K_z. Michl and Thulstrup have experimentally measured the orientation factors for a range of molecules that may be related to styrene sulfonate [12].

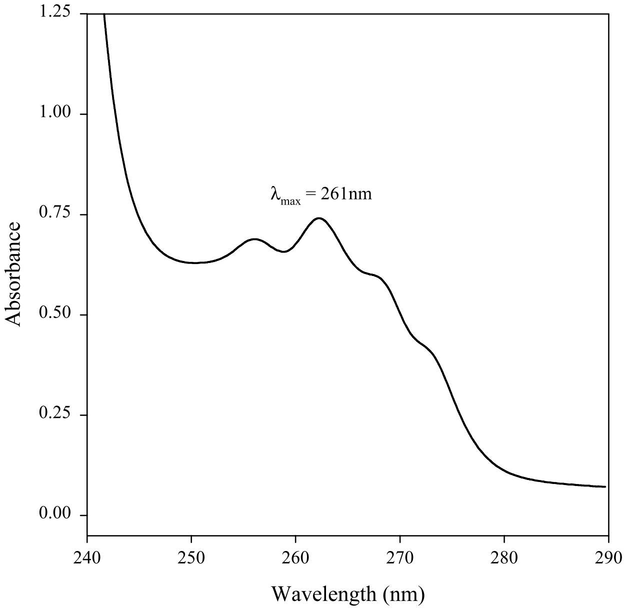

Fig. 1. Ultra violet absorption spectrum for PSS in triple distilled H_2O showing the λ_{max}, which is the wavelength of light used in subsequent rheo-optic experiments.

In this study, the optical anisotropy of the poly(styrene sulfonate) is characterised by measuring changes in the UV extinction properties of the shear aligned polyelectrolyte in aqueous solution. The conformation effects on the zero shear viscosity and the shear thinning nature of a poly(styrene sulfonate) solution have been studied using steady shear rheological techniques. From the rheological measurements it is possible to assign a relaxation time to the polyelectrolyte in solution that is dependent on the macromolecule environment. The microstructural response and the dichroic ratio of the polyelectrolyte, in solution, to an applied hydrodynamic deformation were measured using spectroscopic techniques. The solvent viscosity, electrolyte concentration and the polyelectrolyte molecular weight effects on the optical properties on the solutions under shear are subsequently discussed.

2. Experimental

2.1. Materials

Samples of sodium poly(styrene sulfonate), PSS, were purchased from Sigma–Aldrich, (Batch No. 13825KR and 00811PY) and from Polymer Laboratories (Batch No. 456335). Gel Permeation Chromatography (GPC) (DAWN, Wyatt Technology) was used to determine the M_w and the polydispersity of the polyelectrolyte system used and are given in Table 1.

2.2. Apparatus

The shear viscosity measurements were conducted using the cone and plate geometry of a Carri Med CSL^{2}100 Controlled Stress Rheometer.

The UV absorbance spectra were collected using a Cary 3E UV–Vis Spectrophotometer over a wavelength range of 300–190 nm. The UV absorption spectrum, given in Fig. 1, shows a peak at 261 nm, λ_{max}, which attributed to the absorption and scattering of the styrene sulfonate groups. This has been shown by subtracting the predicted scattering curve from the measured absorption spectrum [13]. The observed increase in extinction at lower wavelengths is attributed to scattering only. All rheo-optic experiments were performed at $\lambda = 261$ nm.

2.3. Rheo-optic measurement technique

The spectroscopic technique employed uses quartz concentric cylinders [14]. The ratio of the radii of the two quartz cylinders, $K = R_1/R_2 > 0.95$, ensures that a near constant shear rate is maintained across the gap. The

Couette cell is placed in the Cary 3E Spectrophotometer and aligned so the flow field is perpendicular to the incident beam. The incident beam may be polarised by using a Glan–Taylor polariser (CARY, mounted with vernier and dial, extinction ratio 1:10^{-5}) oriented between $\psi = 0°$ (parallel) and $\psi = 90°$ (perpendicular) to the flow field allowing angular dependent extinction changes to be recorded. Baseline spectra for the absorbance due to the polariser were recorded enabling the extinction coefficient of the polariser to be subtracted in subsequent experiments.

The solution is placed in the shear cell and allowed to stand undisturbed. The relative orientation of the polyelectrolyte chain segments is then assumed to be random. The shear cell was loaded into the spectrophotometer with the light beam wavelength set to 261 nm, the absorbance maximum for PSS. A shear rate, between 0 and 2550 s^{-1}, was set for 10 s with the absorbance measured over this time. The cessation of shear was followed by 10 s at zero shear during which time the absorbance was observed to return to the constant pre-shear value, indicating the solution had returned to the isotropic state. The change in absorbance, ΔAbs, due to shear, is characterised using

$$\Delta\mathrm{Abs} = \frac{A_{\mathrm{Shr}} - \dfrac{(A_{\mathrm{Pre}} + A_{\mathrm{Post}})}{2}}{\dfrac{(A_{\mathrm{Pre}} + A_{\mathrm{Post}})}{2}} \tag{1}$$

where A_{Pre} is the average pre-shear absorbance, A_{Post} is the average post-shear absorbance and A_{Shr} is the average shear absorbance. As the concentration and path-length remain constant throughout the experiment any changes to the absorbance may be attributed to changes in the extinction coefficient or projected cross sectional area of the chain segment. By use of the Beer Lambert Law, where Abs $\propto \epsilon$, for constant concentration and path-length, the change in absorbance value will be the same as that for the change in extinction coefficient, $\Delta\epsilon$, termed the reduced change in extinction coefficient. This procedure was used for each of the measured solutions. It should be noted that the reduced change in extinction coefficient is angularly dependent as is discussed later with reference to Eq. (4).

3. Results and discussion

3.1. Characterisation of the test solutions

The solutions used in the rheo-optic experimentation comprised of 36 mg ml^{-1} sodium poly(styrene sulfonate), PSS, with different M_w solubilised in solutions of glycerol–water and glycerol–salt (NaCl). At this concentration of PSS all solutions used in this study are above the critical overlap concentration, c^*, as calculated using the polyelectrolyte chain and solution parameters in Eq. (2) [2]. It has been reported that for regions of high polyelectrolyte concentration, the polyelectrolytes begin to behave in a manner similar to neutral polymers where electrostatic interactions need no longer be considered [15]. The test solutions used in this study are below this higher concentration as electrostatic considerations are still seen to have an effect on the solution properties. The critical overlap concentration is given as

Table 2
Solution properties for PSS, $M_w = 1500$ kg mol^{-1}, in glycerol salt solutions. The persistence length, L_P, is the sum of the intrinsic and electrostatic persistence lengths. c^* and R were calculated using Eqs. (2) and (3), respectively

Glycerol–NaCl (M)	L_P (nm)	c^* (mg ml^{-1})	R (nm)
0	1.20	3.02	390
0.01	1.17	3.25	380
0.1	1.07	4.51	360
1	1.01	8.36	310

$$c^* \cong \frac{m_0}{aN_A} L^{-(4/5)} (L_P\lambda_D)^{-(3/5)} \tag{2}$$

where m_0 is the monomer molecular weight, a the monomer length, N_A the Avogadro number, L the contour length, L_P the persistence length and λ_D the Debye length. Eq. (3) describes the overall radius of the polyelectrolyte chain, R, in the semi-dilute region for an electrolyte solution where the assumption for the Flory radius is no longer valid [2],

$$R \cong \left(\frac{m_0}{aN_A}\right)^{(1/8)} (L_P\lambda_D)^{(1/8)} L^{(1/2)} c^{(-1/8)} \tag{3}$$

The radius, R, from Eq. (3) approximates the end-to-end distance for the polyelectrolyte chain in an electrolyte solution. Eqs. (2) and (3) are valid for systems of added electrolyte. For the test solutions with no added electrolyte the presence of the counter ions, and therefore the Debye length, is not accounted for in the calculation of the polyelectrolyte solution parameters [15]. The total concentration of counterions at 36 mg ml^{-1} is 0.15 M. Conductivity measurements, not reported here, indicate that the sulphate groups are only 10% dissociated. This indicates that the concentration of counterions is approximately 0.015 M at the polyelectrolyte concentration of 36 mg ml^{-1} [13]. Therefore, the c^* and radius for the polyelectrolyte chain, with counter ions, in the salt free solution was calculated using Eqs. (2) and (3).

The radius for the polyelectrolyte chain remains unchanged with changing solvent viscosity or with the inclusion of the Debye length into the calculation at 0 and 0.01 M NaCl. Table 2 shows the dramatic effect the electrolyte concentration has on reducing the chain radius above 0.01 M NaCl. The reduction in chain dimensions with the addition of salt is due to the shielding of the electrostatic repulsions allowing the coil to become more compact.

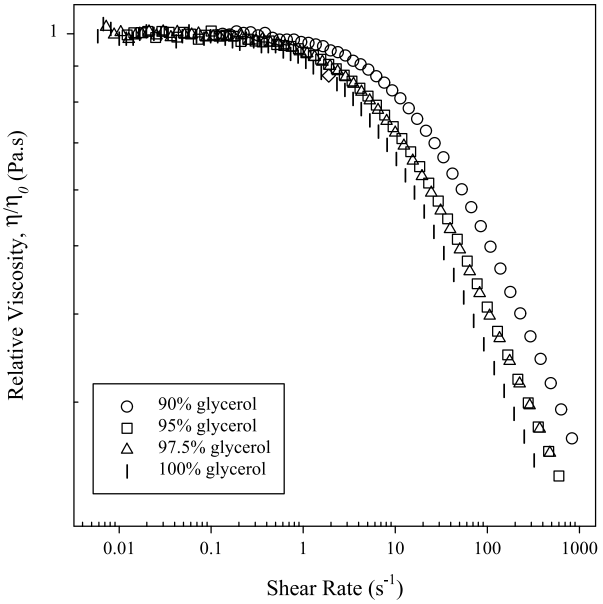

Fig. 2. The relative shear viscosity, η/η_0, data for 36 mg ml^{-1} PSS (M_w 1500 kg mol^{-1}) in glycerol–water solutions.

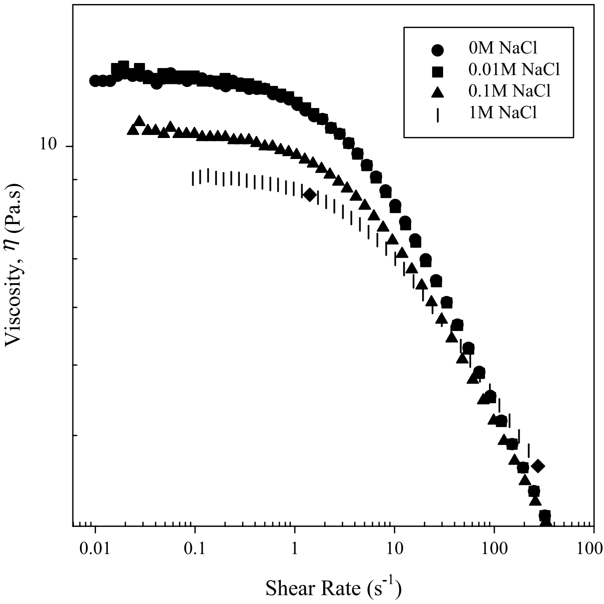

Fig. 3. The shear viscosity, η, data for 36 mg ml^{-1} PSS (M_w 1500 kg mol^{-1}) in glycerol–electrolyte (NaCl) solutions.

3.2. Rheology of the test fluids

By way of shear stress, the effect of solvent viscosity and electrolyte concentration on the state of the polyelectrolyte in solution may be quantified. The polyelectrolyte relaxation time, τ, was approximated from these measurements. The relaxation time is determined from when the applied strain rate alters the conformation of the polyelectrolyte. In the quiescent state the macromolecules have a given conformation, which it maintains at low shear rates. When the applied shear rate reaches a critical level, the restoring forces within the polyelectrolyte are unable to return the molecule to the equilibrium conformation before another perturbation in the local hydrodynamic environment. Simplistically, this leads to a change in conformation with the major axis of the deformed macromolecule aligned in the direction of flow and, therefore, a reduction in the solution viscosity [16]. The relaxation time of the polyelectrolyte is dependent on the solvent properties with the onset of shear thinning being observed at different shear rates for solutions of differing solvent composition.

The polyelectrolyte relaxation time was determined from the shear flow curves, Figs. 2 and 3, and defined as the inverse of the shear rate, $\dot{\gamma}_C$, at which the solution begins to shear thin [17]. The onset of shear thinning was determined from when the solution viscosity had been reduced to 95% of the zero shear viscosity. The relaxation time, τ, may be used to normalise the shear rate, removing the polyelectrolyte relaxation time from the applied deformation. The reduced shear rate, β, is defined as$\beta = \tau \times \dot{\gamma}$. The reduced shear rate will be used later in this discussion to analyse the shear spectroscopy results. The relaxation time for a concentrated PSS solution was found to scale with M_w^3, as expected for the relaxation of a chain in a semi-dilute solution [10,17–19]

The power law model was used to approximate the shear-thinning region of the polyelectrolyte solutions. For solutions of different viscosity the power law exponent, n_s, remains relatively constant about an average value of 0.25, indicating the solvent viscosity has no effect on the extent of shear thinning. For solutions of added electrolyte the size of the coil is reduced and the molecule adopts a tighter conformation. The power law exponent for the electrolyte solutions is shown to decrease with added salt for [NaCl] > 0.01 M, leading to a crossover region in the solution viscosities at high shear rates. This result is consistent with the electrolyte suppressing the molecular dimensions and therefore the extent of conformational change due to shear, i.e. shear thinning [20]. The change in power law behaviour may be explained by a transition from an extended conformation, which is more shear thinning, to a "worm-like" or compact random coil conformation with the addition of salt. It was not possible to measure any power law coefficients for the low M_w PSS due to the lack of a significant shear-thinning region over the shear rate range tested.

4. Shear spectra with unpolarised light

4.1. Effect of solvent viscosity

The extinction coefficient in the quiescent state was shown to be independent of solvent viscosity (glycerol/water ratio). Fig. 4 shows the reduced change in extinction coefficient, calculated by Eq. (1), as a function of wavelength,

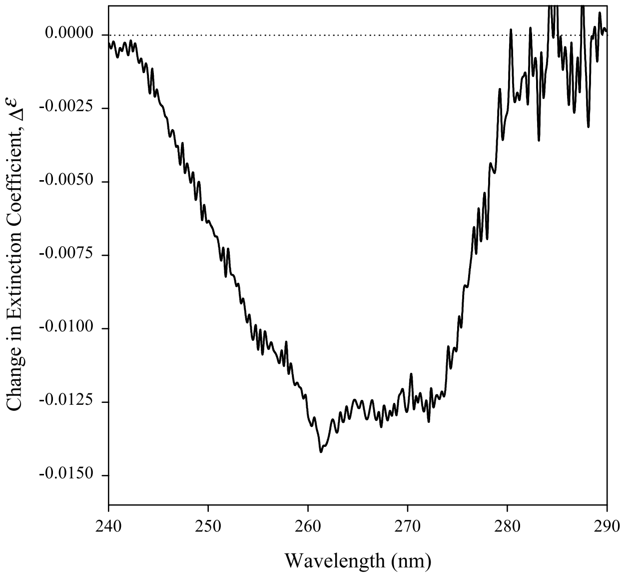

Fig. 4. Shear spectrum, at $1525\ \mathrm{s}^{-1}$, for $36\ \mathrm{mg\ ml}^{-1}$ PSS (M_w $1500\ \mathrm{kg\ mol}^{-1}$) in pure glycerol. The greatest change in extinction coefficient is seen at $\lambda_{\max} = 261$ nm.

λ, for $1500\ \mathrm{kg\ mol}^{-1}$ PSS in 100% glycerol at a shear rate of $1525\ \mathrm{s}^{-1}$. The maximum $\Delta\epsilon$ was observed at $\lambda = 261$ nm. The rheo-optic measurements were conducted for all test solutions at the $\lambda_{\max} = 261$ nm for PSS in glycerol. Fig. 5 is an example of the absorbance data obtained for the $36\ \mathrm{mg\ ml}^{-1}$ PSS in 100% glycerol, whilst changing the shear rates. The shear rates used in this experiment are detailed in Fig. 5.

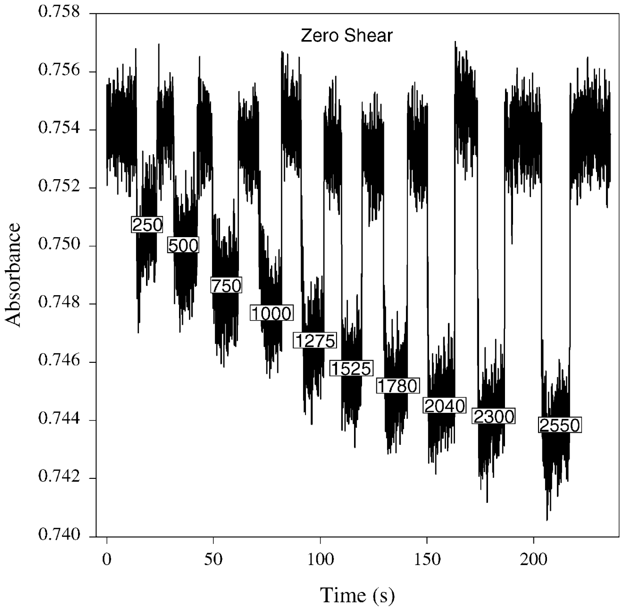

Fig. 5. Shear spectroscopy data for $36\ \mathrm{mg\ ml}^{-1}$ PSS (M_w $1500\ \mathrm{kg\ mol}^{-1}$) in pure glycerol at $\lambda_{\max} = 261$ nm. The change in absorbance is taken as the difference between the absorbance of the quiescent state and the absorbance of the sheared solution. The applied shear rate is shown for each spectral change.

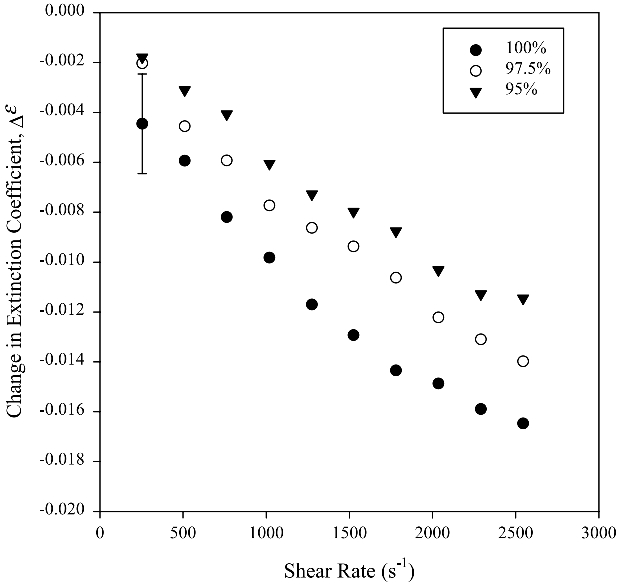

Fig. 6. The change in the reduced change in extinction coefficient, $\Delta\epsilon$, with unpolarised light for $36\ \mathrm{mg\ ml}^{-1}$ PSS (M_w $1500\ \mathrm{kg\ mol}^{-1}$) in glycerol–water solutions. The sample error bars are derived from the experimental noise, as observed in Fig. 5, and are relevant for all subsequent measurements.

The reduced change in extinction coefficient, $\Delta\epsilon$, for each applied shear rate is plotted in Fig. 6. The test solutions for the solvent compositions as shown were measured. It was found that for glycerol concentrations of 90% (w/w) the change in extinction was not measurable within the experimental error. Each set of results shows a systematic decrease in the absorbance, where the absorbance is dependent on the applied shear. A sample error bar appropriate for the entire set of results is shown.

The effect of the solvent composition on the reduced change in extinction coefficient may be due to changes in the solvent quality or purely viscous effects. By plotting the change in extinction versus a 'solvent' shear stress, i.e. $\sigma = \dot{\gamma} \times \eta_s$, solvent viscosity effects are removed, Fig. 7. All data points are now effectively normalised to a single curve, within experimental error, for the three solutions. This shows that the orientation of the polyelectrolyte chain segments, and therefore the $\Delta\epsilon$, is identical for all solutions at a given shear stress. Alternatively we may have taken solvent viscosity effects into account by plotting $\Delta\epsilon$ versus β. However, due to the extra experimental errors introduced in finding the relaxation time for the different solvent viscosities, the reduced shear rate was not used to normalise $\Delta\epsilon$ in this case.

The rheo-optic experiments described have been conducted at $\lambda_{\max} = 261$ nm, where the attenuation of light results from both scattering and absorption phenomena. The effect of absorption on the reduced change in extinction coefficient may be removed by conducting the experiment in a wavelength region where scattering is the only attenuating mechanism. Further shear spectroscopy measurements were performed where the wavelength of

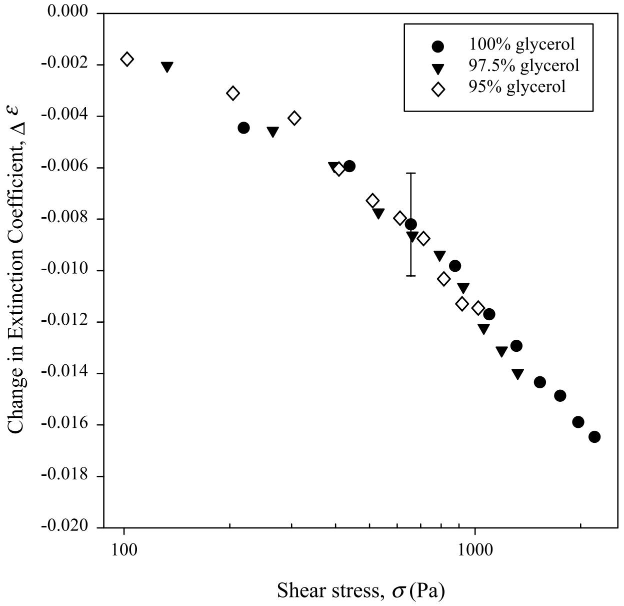

Fig. 7. The reduced change in extinction coefficient, $\Delta\epsilon$, as calculated by Eq. (1), with unpolarised light for 36 mg ml^{-1} PSS (M_w 1500 kg mol^{-1}) in glycerol–water solutions verses the shear stress, σ.

the incident beam was shifted to 245 nm. As with the change in extinction including absorption the scattering cross section is reduced with the application of shear, seen in Fig. 8.

4.2. Effect of the addition of salt (NaCl)

The polyelectrolyte cross sectional area is reduced with the addition of salt resulting in a reduction in the extinction coefficient or orientation with the shear field. The electrolyte effect is also seen in the relaxation time data with a reduction in the longest relaxation time with increasing salt concentration (see Figs. 2 and 3). The reduced change in extinction coefficient, $\Delta\epsilon$, versus the reduced shear rate, β, for the added salt solutions is plotted in Fig. 9.

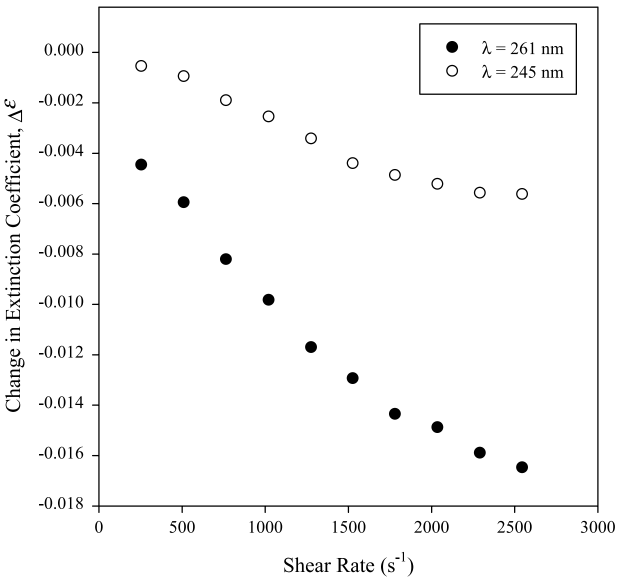

Fig. 8. The reduced change in extinction coefficient, $\Delta\epsilon$, with unpolarised light for 36 mg ml^{-1} PSS (M_w 1500 kg mol^{-1}) in glycerol solutions at $\lambda = 245$ nm, where the extinction of light arises from scattering alone, and $\lambda = 261$ nm, where the extinction arises from a combination of scattering and absorption.

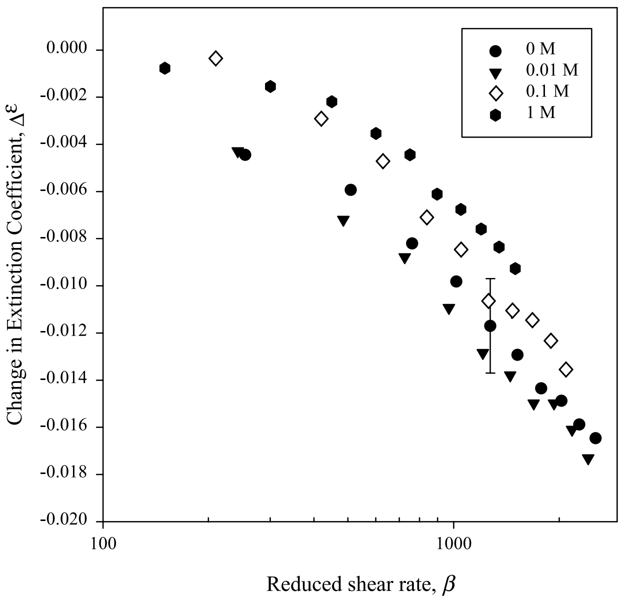

Fig. 9. The reduced change in extinction coefficient, $\Delta\epsilon$, with unpolarised light for 36 mg ml^{-1} PSS (M_w 1500 kg mol^{-1}) in glycerol–electrolyte solutions verses the reduced shear rate, β.

4.3. Effect of molecular weight

The molecular weight dependence of $\Delta\epsilon$ for PSS in glycerol during shear is shown in Fig. 10. The results for $\Delta\epsilon$ against β highlight the large discrepancy between the relaxation time for the test solutions of PSS of different M_w. The small relaxation time of the 360 kg mol^{-1} polyelectrolyte in glycerol leads to a reduced ability of the hydrodynamic force to orient to the chain segments and therefore a smaller $\Delta\epsilon$.

In summary, for the entire set of test conditions studied $\Delta\epsilon$ was shown to decrease, increase negatively, with shear for unpolarised UV light. The extinction of light by the polyelectrolyte in solution arises from the interaction of light with the styrene sulfonate groups of the macromolecule backbone. In quiescent solution the segments adopt a random orientation and the extinction coefficient of the polyelectrolyte in solution is then measured. Upon the addition of shear the polyelectrolyte backbone segments orient in the plane of shear and leading to an increase in the ordering of the polyelectrolyte chains. For each segment of the polyelectrolyte chain the average extinction cross section is greater in the quiescent state than for the aligned sample. In the quiescent state, the plane containing the styrene sulfonate group perpendicular to the backbone may adopt a random orientation, therefore have an average extinction

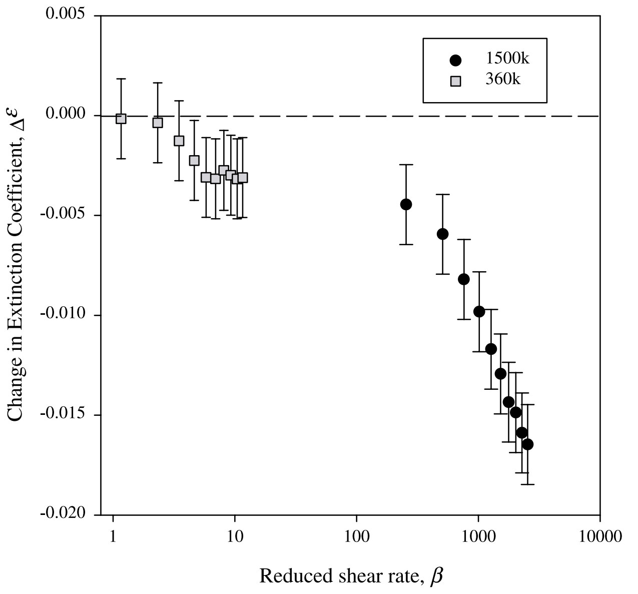

Fig. 10. The reduced change in extinction coefficient, $\Delta\epsilon$, with unpolarised light for 36 mg ml^{-1} PSS of different M_w in glycerol solutions verses the reduced shear rate, β.

cross section. With the application of shear to the polyelectrolyte backbone the backbone aligns in the direction of shear with the styrene sulphonate groups oriented perpendicular to the shear direction as shown in Fig. 13(c). When the polyelectrolyte backbone is aligned, the styrene sulphonate groups will map out a disk which is oriented perpendicular to the shear direction and in the plane of $\langle\epsilon\rangle_{\psi}$, thus the resultant negative and positive changes in extinction for polarised light. See Eq. (4) and explanation. In this experiment the shear direction is perpendicular to the light beam [13]. Therefore, the induced alignment of the polyelectrolyte results in a reduction in the extinction cross sectional area of the polyelectrolyte, reducing the extinction coefficient with shear as shown in Fig. 9.

5. Shear spectra-polarised light

The angle of polarization, ψ, of the incident light was controlled as previously discussed. All the experiments thus far have shown the reduced change in the extinction coefficient of the PSS in solution to be reduced by the application of shear. The use of polarised light may provide further detail of the reduced change in extinction coefficient change and the orientation of the chain segments to the direction of shear.

For the test solution of PSS in pure glycerol the angular dependence of the reduced extinction coefficient on the applied shear rate was measured, Fig. 11. The greatest reduction, increase negatively, in the reduced change in extinction coefficient was seen for the light was polarised in the direction of the shear (i.e. $\psi = 0°$). As the angle of the polarised light was increased from $\psi = 0°$ through to $\psi = 90°$ the $\Delta\epsilon$ was seen to go through a transition point where the extinction of the chain segment under the hydrodynamic force is the same as the extinction of the segment in the quiescent state, i.e $\Delta\epsilon = 0$. This result is highlighted in Fig. 12 where the $\Delta\epsilon = 0$ for the light polarised at $\psi = 67°$ for all shear rates measured. The $\Delta\epsilon$ continued to increase to a maximum for when the polarisation orientation angle is $\psi = 90°$ (perpendicular to the shear direction).

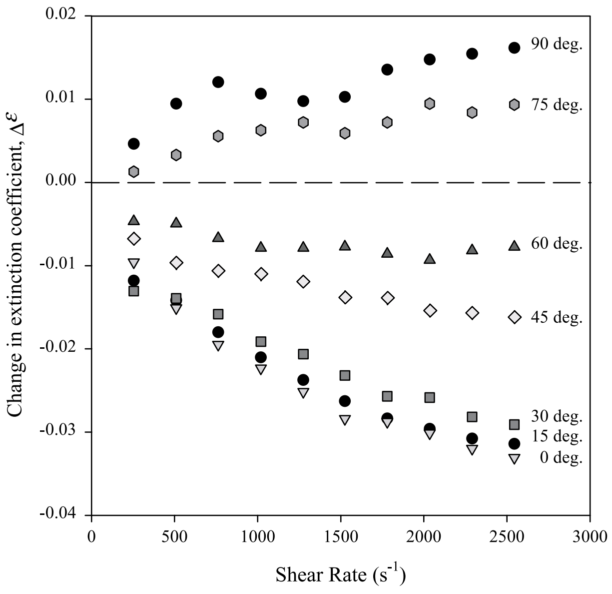

Fig. 11. The reduced change in extinction coefficient, $\Delta\epsilon$, for 36 mg ml^{-1} PSS (M_w 1500 kg mol^{-1}) in glycerol verses shear rate for changing the angle of the polarised incident light, ψ, to the direction of shear.

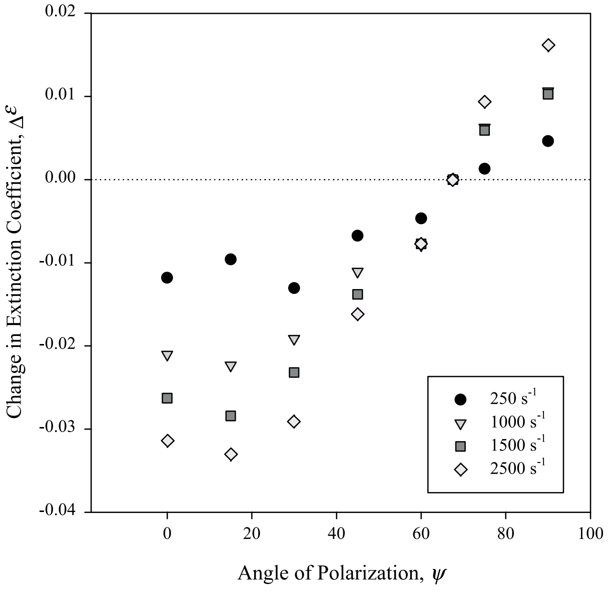

Fig. 12. The reduced change in extinction coefficient, $\Delta\epsilon$, for 36 mg ml^{-1} PSS (M_w 1500 kg mol^{-1}) in glycerol verses the angle of the polarised incident light, ψ, to the direction of shear for the different shear rates as shown.

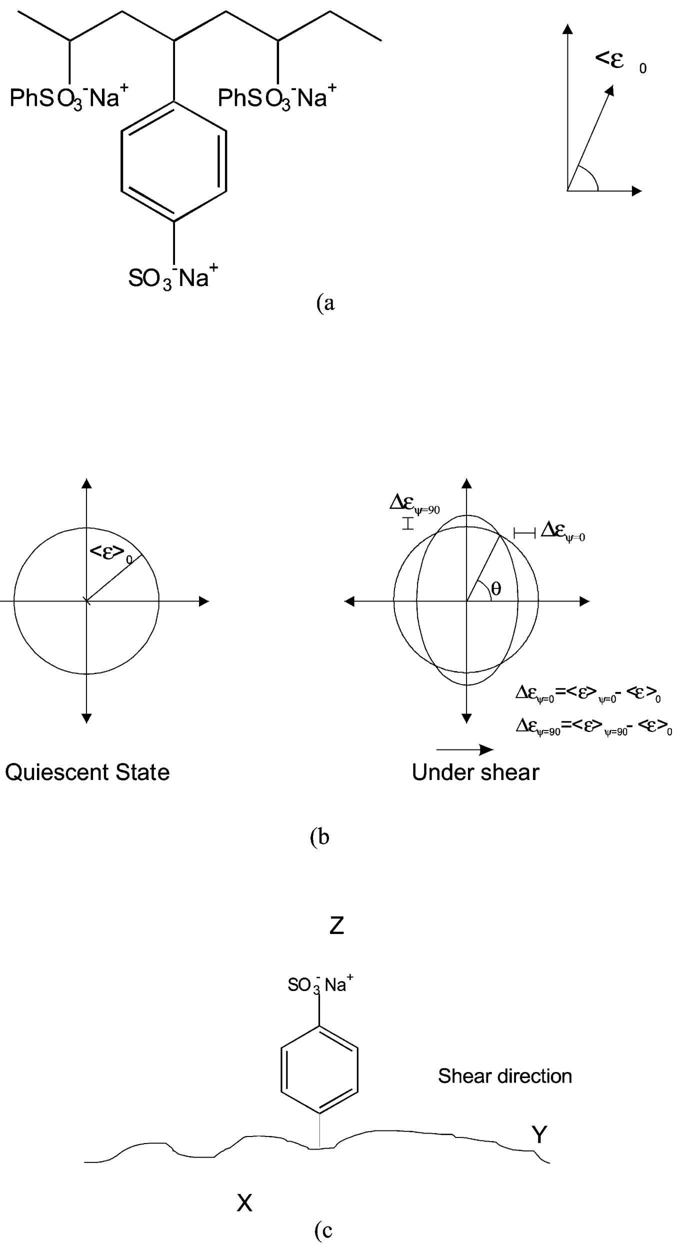

Fig. 13. The origin of the extinction coefficient for the styrene sulphonate monomer unit (a). ϵ_1 and ϵ_2 are the principal axes extinction coefficients and $\langle\epsilon\rangle_0$ is the average extinction coefficient. Part (b) shows the origin of the measured changes in the extinction coefficient. Part (c) shows the proposed axes used in defining the orientation factors, K_u, as described by Michl and Thulstrup [15]. The incident light beam is projected onto the *yz* plane, along the *x*-axis.

The significance of $\Delta\epsilon = 0$ at $\psi = 67°$ will now be discussed. In the quiescent state the polyelectrolyte chain has an average extinction coefficient, $\langle\epsilon\rangle_0$, at an angle θ to the polyelectrolyte backbone. The magnitude of $\langle\epsilon\rangle_0$ may be calculated from the average of the extinction coefficients along the principal axes of the styrene sulfonate side group, ϵ_1 and ϵ_2, and is approximately equal to $\langle\epsilon\rangle_0 = 1/3(\epsilon_1 + 2\epsilon_2)$. The origin of the principal extinction coefficients is shown in Fig. 13(a), where ϵ_1 is parallel and ϵ_2 is perpendicular to the polyelectrolyte backbone. The average extinction coefficient in the quiescent state, $\langle\epsilon\rangle_0$, is independent of ψ. This was determined experimentally for an equilibrium solution.

Upon the application of shear to the polyelectrolyte system a major proportion of the backbone aligns in the shear direction. The change in extinction coefficient at the quiescent state, $\langle\epsilon\rangle_0$, compared to that under shear, $\langle\epsilon\rangle_\psi$ (at angle of light polarisation, ψ), may be represented by

$$\Delta\epsilon_\psi = \langle\epsilon\rangle_\psi - \langle\epsilon\rangle_0 \tag{4}$$

For $\psi = 90°$, where ϵ_2 is essentially being measured, $\Delta\epsilon_{\psi=90°} > 0$ as $\langle\epsilon\rangle_0 < \langle\epsilon\rangle_{\psi=90°}$, where $<\epsilon>_{\psi=90°}$ is the average extinction coefficient for the polyelectrolyte solution under shear for $\psi = 90°$. By the same argument, for when $\psi = 0°$, $\Delta\epsilon_{\psi=0°} < 0$ as $\langle\epsilon\rangle_0 > \langle\epsilon\rangle_{\psi=0°}$, where $\langle\epsilon\rangle_{\psi=0°}$ is the average extinction coefficient for the polyelectrolyte solution under shear for $\psi = 0°$. When the incident light is polarised at 67° to the direction of shear the measured $\Delta\epsilon_{\psi=67°} = 0$, leading to the conclusion that $\langle\epsilon\rangle_0 = \langle\epsilon\rangle_{\psi=67°}$. A schematic view of the measured extinction changes is given by Fig. 13(b). From the experimental data we can conclude that the angle of the average extinction coefficient between ϵ_1 and ϵ_2, θ, is then approximately 67° and the dichroic ratio ϵ_2/ϵ_1 is equal to tan 67° or approximately 2.35. In addition, the ratio of the absolute changes in magnitude of extinction, $|\Delta\epsilon_{\psi=0°}|/|\Delta\epsilon_{\psi=90°}| \approx 2.35$, also corresponds to the dichroic ratio.

The orientation factors, K_u, for styrene or styrene sulfonate were not measured by Michl and Thulstrup [12]. In order to compare the work of Michl and Thulstrup with this study we have chosen a compound of similar chemical structure to styrene sulfonate to approximate its orientation factors. The compound chosen was 4-dimethyl-amino-benzene, which has the orientation factors of $K_z = 0.56$, $K_y = 0.25$, $K_x = 0.19$ as measured by Michl and Thulstrup [12]. We propose that the orientation factors are equivalent to the dichroic ratio by the relationship $\epsilon_2/\epsilon_1 = 2K_z/(K_y + K_x)$, which for 4-dimethyl-amino-benzene is equal to 2.5. The average value of K_y and K_x is used to account for the rotation of the styrene sulfonate group about the z molecular axis, which is perpendicular to the polyelectrolyte backbone.

For the ordered styrene sulfonate groups, where the yz plane of the benzene ring is aligned in the direction of shear, as shown in Fig. 13(c), the dichroic ratio would be approximated by $K_z/K_y = 2.3$. This ratio is comparable to the experimentally measured value of the dichroic ratio of 2.35 found in this study. It is therefore possible to relate the orientation factors, determined from the compound in stretched solid films, to the dichroic ratio for the styrene sulfonate group in solution, where the alignment of the styrene sulfonate groups is induced by shear.

6. Conclusions

The solution properties of sodium poly(styrene sulfonate), PSS, in glycerol have been characterised by optical and rheological methods. The relaxation time for each solution was measured and shown to depend on the solution viscosity, electrolyte concentration and polyelectrolyte molecular weight, M_w. The rheo-optic experiments indicated the PSS chains in solution align with the direction of shear. This was confirmed by the use of polarised incident light in the rheo-optic set up where the reduced change in extinction coefficient was seen to decrease under shear for light polarised in the direction of shear, and increase for light polarised perpendicular to shear. The extinction of light arises from the styrene sulfonate groups oriented perpendicular to the backbone. The ratio of extinction coefficients for the principal axes of the aligned polyelectrolyte and therefore the ratio of polarisabilities, can be related to the angle of polarisation, ψ, that gives rise to $\Delta\epsilon_\psi = 0$ under shear. This technique may be applied to other macromolecular chains that contain a polarisable monomer unit where the overall average dichroic ratio of the monomer group, under shear, simply corresponds to tan ψ for $\Delta\epsilon_\psi = 0$.

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