

J. A. Odell
S. J. Haward

Viscosity enhancement in non-Newtonian flow of dilute aqueous polymer solutions through crystallographic and random porous media

Received: 13 June 2005
Accepted: 22 September 2005
Published online: 9 December 2005
© Springer-Verlag 2005

J. A. Odell (✉) · S. J. Haward
H.H. Wills Physics Department,
University of Bristol,
Tyndall Avenue,
Bristol BS8 1TL, UK
e-mail: jeff.odell@bristol.ac.uk
Tel.: +44-117-9288717
Fax: +44-117-9255624

Abstract We report results on the flow of dilute aqueous solutions of hydrolysed poly(acrylamide) (HPAA) through beds of spheres packed in simple cubic and body-centred cubic crystallographic arrays. Pressure drop measurements made across the arrays as a function of the flow rate have been used to estimate the specific viscosities of the HPAA solutions as a function of the superficial strain rate. It is found that greater non-Newtonian increases in the specific viscosity occur in the body-centred cubic array, which is thought to be due to the presence of trailing stagnation points, which are not present in the simple cubic array. Experiments have been

performed using HPAA solutions in the presence of mono- and divalent cations at various concentrations and, for validity, have been compared with results obtained from a traditional randomly packed porous medium. In addition, a study of mechanical degradation of the polymer in flow through the crystallographic arrays has been carried out and reveals a greater rate of degradation in the body-centred array and also a significant increase in degradation with salt concentration.

Keywords Porous media · Extensional flow · Stagnation point · Viscosity

Introduction

In many practical flow situations, solutions of flexible polymers are found to exhibit a well-known non-Newtonian viscosity enhancement effect. This is likely to be due to extensional components in the flow field, which can cause flexible polymer molecules to stretch and orientate, causing an increase in the extensional viscosity. This viscosity enhancement is important in many industrial applications, including food technology, paint and cosmetic formulation, and enhanced oil recovery (EOR).

Potential EOR applications based upon polymer solution flooding depend upon studies of porous media flow of polymer solutions in order to optimise the use of polymers as additives in the solutions used for oilfield flooding. One essential ingredient is the achievement of effective viscosity matching at the oil–solution interface. Remarkably, this can be achieved with low concentrations of ultra high molecular weight flexible polymers [such as poly(acrylamides) (PAA)]

in brine. However, the large viscosity enhancement that occurs when polymer solutions flow through porous media, which can be exploited for EOR, is not well understood, mainly due to difficulties defining the complex random geometry of the flow field and probing the molecular response of the polymers within the porous medium. Also the use of the polyelectrolyte hydrolysed poly(acrylamides) (HPAA) in order to further increase the solution viscosity through increased coil expansion raises interesting questions regarding the interactions that may occur between the polymer and divalent or multivalent ions present in the brine.

Since porous media are generally modelled in the laboratory by beds packed with spheres or ballotini, it is important to understand how polymer solutions flow around spheres in order to appreciate the complexities of flow through porous media at the particle level. In a preceding article (Haward and Odell 2004), we have utilised model solutions of atactic polystyrene in dioctyl phthalate (aPS in DOP) to examine the problem of flow around both single

spheres and around two spheres aligned in the flow direction. The latter experiment gives insight into the interactions that occur between the particles forming a model porous media matrix. Additionally, the same model aPS/DOP solutions have been studied in flow through crystallographic porous media (Haward and Odell 2003), which will be seen to provide a valuable comparison with the current work.

In this paper we present results from the flow of HPAA solutions (also in the presence of mono- and divalent salts) through two crystallographically packed porous media for comparison with the results obtained for randomly packed porous media. The two regular porous media have simple cubic (SC) and body-centred cubic (BCC) packing of spheres, so the geometries are contrasting in that the former does not contain trailing stagnation points in the flow direction (along the cube sides), while the latter has a trailing stagnation point associated with every sphere within the lattice. By studying flow through these geometrical constructions we hope to elucidate the mechanism by which the viscosity enhancement occurs, i.e. through periodic contractions in flow from pore to pore or through the high velocity gradient that is present in the locality of trailing stagnation points.

Background

There is a large body of literature on porous media flow of polymer solutions. One of the most interesting and studied aspects of the flow of polymer solutions through porous media is the non-Newtonian increase in flow resistance, which occurs for flexible polymers when a critical flow rate is exceeded. Among the first to observe this effect using randomly packed beds of spheres were Dauben and Menzie (1967) and Marshall and Metzner (1967). James and McLaren (1975), with dilute aqueous solutions of poly(ethylene oxide) (PEO), concluded that an increase in the extensional viscosity of the polymer solution in the pore-spaces is essential to explain the critical increase in flow resistance.

Durst et al. (1981) have performed extensive studies of the flow of PAA and HPAA solutions through porous media investigating the effects of polymer concentration, solvent quality and degree of hydrolysis on the excess pressure drop. In addition the effect of changing the ionic environment of the HPAA solutions using NaCl was studied, which is highly analogous to changing the solvent quality. As the ionic strength is increased the polymer molecules become more randomly coiled due to screening of the like charges attached to the polymer backbone. Durst et al. (1981) found that this caused the low Reynolds number limit of the flow resistance to be reduced to the Newtonian value, while the onset of non-Newtonian behaviour became increasingly critical. This strongly suggests that a coil \leftrightarrow stretch transition of the type predicted by de Gennes (1974) and Hinch (1977) may be responsible for the increase in flow resistance through an increase in extensional viscosity of the polymer solution.

Durst et al. (1981) also performed some experiments on the effects of the divalent salts CaCl₂ and MgCl₂ on HPAA solutions. At a given ionic strength the divalent salts were found to have a much greater effect on the flow resistance of the solutions than NaCl. The authors concluded that while the monovalent salt simply screens the free charges on the polymer molecule, the divalent salts also influence the hydrodynamic dimensions of the molecule.

Kulicke and Haas (1984) have studied the effects of size of the particles used to pack the porous media as well as molecular weight, concentration and solvent quality on the behaviour of PAA solutions. The authors found that the molecular weight of the polymer had a significantly greater effect on the onset Reynolds number, Re_o , than the concentration. They also found Re_o to be inversely proportional to the relaxation time of the fluid. With increasing particle diameter, the authors found a shift in Re_o to higher values but no change in the maximum value of flow resistance. This is also strong evidence to indicate that the coil \leftrightarrow stretch transition is the cause of the enhanced flow resistance.

A study of the flow of ultra high molecular weight PAA solutions ($M_w=18.2\times 10^6$ in ethylene glycol) through regularly packed beds has been undertaken previously by Haas and Durst (1982). Orthorhombic and cubic arrangements of spheres were constructed. However, it should be noted that neither arrangement presented trailing stagnation points in the flow direction. The authors noted that the strain in a given "pore" was small (~ 5 for the cubic cell). The specific flow resistance was measured as a function of flow rate for different numbers of repeat unit cells, finding a progressive increase over the passage of fluid through up to four unit cells, followed by a reduction for further repeats. The authors speculated that the molecular strain must increase as fluid elements pass from one pore to the next. The reduction in resistance coefficient for passage through more than four pores is likely due to extensional thermo-mechanical degradation of the ultra high molecular weight polymers.

The authors attempted to define the critical Deborah number corresponding to the flow rates at the onset of the increase in flow resistance from Zimm relaxation times calculated for the PAA system. They derived a numerical factor for each geometry to relate the observed superficial Deborah number with that derived from the calculated Zimm relaxation time. They observed that the unscaled Deborah numbers were much lower than the expected value of ~ 0.5 .

Interestingly, the flow resistance in a randomly packed bed was equivalent to a linear superposition of the flow resistance through the two regularly packed beds. The authors explained this by the observation that a random arrangement of spheres can be thought of as a random superposition of regular unit cells. However, the result remains surprising since neither of the regularly packed beds contained any trailing stagnation points, which must necessarily be present in any random packing of spheres.

Saez et al. (1994) reported observations of non-Newtonian extensional flow effects coupled with birefringence in

porous media flow of solutions of monodisperse atactic poly(styrene) of $M_p=12.25 \times 10^6$ and $c=0.08\%$, well below the conventional overlap concentration c^* . The authors argued that the non-Newtonian effects observed in porous media flow are best explained by the formation of transient networks of entangled molecules, a theory first proposed by Odell et al. (1988a) to account for the highly critical nature of the viscosity increases observed with poly-disperse polymer solutions.

However, our recent study of highly dilute solutions of monodisperse atactic poly(styrene) ($6.9 \times 10^6 \leq M_w \leq 10.2 \times 10^6$ and concentration as low as 0.005%, or $\sim c^*/40$) in flow through regularly packed beds (SC and BCC) strongly suggests that formation of entanglement networks is an unlikely explanation for the flow resistance increase (Haward and Odell 2003). As in the study of Haas and Durst (1982), it was found that the viscosity increase occurred at an anomalously low value of Deborah number, calculated using the Zimm relaxation time and a strain rate based on the particle size of the porous array. Also, surprisingly, larger non-Newtonian increases in solution viscosity were measured in the SC than in the BCC array, despite the absence of stagnation points in the former. However, these observations are explained by the periodic changes in pore volume in the arrays, which contribute a significant factor to the strain rate and is actually greater in the SC structure. We believe that macromolecules can accumulate strain in flow through successive pores due to hysteresis in the extension/relaxation process predicted by de Gennes (1974). Also it is speculated that non-equilibrium (or pre-stretched) random coil conformations may play an important role since they would extend at a low strain rate and would require a smaller strain to full extension. In porous media there are many opportunities for non-equilibrium conformations to present themselves at pore entrances. Due to the high dilution of the solutions studied, Haward and Odell (2003) firmly attribute the viscosity increase in porous media flow solely to the coil \leftrightarrow stretch transition as envisioned by de Gennes.

In this paper we study the flow of aqueous solutions of ultra high molecular weight HPAAs through regularly packed porous media. We assess the effect of the chain conformation by the addition of NaCl and CaCl₂ to the solutions. Also we study thermomechanical degradation of the polymer in the SC and BCC porous media with and without salts. For validity we see how the results from the regularly packed porous media can be applied to randomly packed porous media.

Experiments

The crystallographic porous media cells were constructed with 4-mm-thick sheet soda glass walls to form square cross-section rectangular boxes of $\sim 30 \times 30 \times 200$ mm to accommodate simple cubic (SC) and body-centred cubic

(BCC) arrays of spheres. The cells were packed by hand with soda glass spheres of diameter 5 ± 0.02 mm, which were supplied by Sigmund-Lindner of Germany. Some of the spheres had to be glued into position to prevent the arrays from collapsing during the construction, although this was kept to a minimum to avoid significant modifications to the porosities of the flow cells. The porosities, ϕ , were calculated from the known volume of the flow cells and the known number of spheres that they contained. These were found to be $\phi=0.476$ for the SC array and $\phi=0.32$ for the BCC array. As previously explained, the geometries of the sphere arrays differed greatly in that the SC contained no trailing stagnation points in the flow direction while the BCC contained a stagnation point for each sphere within the array. The geometries are described more fully, with calculations for the rates of shear and extension in the pores, in a previous publication (Haward and Odell 2003).

The random porous media consisted of a Perspex cylinder of diameter 2.02 cm and length $L=30.37$ cm, which contained a disordered packing of glass ballotini of diameter $d=1.11$ mm. The porosity of the porous medium was measured to be $\phi=0.36$.

The crystallographic porous media were incorporated into a vacuum-driven flow system and the flow through the random porous media was generated by pressurising the solution reservoir with N₂ gas. Both systems produced steady and non-pulsatile flows and minimised mechanical degradation of the polymer solutions, which might have occurred with a pump. In both systems the flow rate of the polymer solution through the porous media was varied by controlling the vacuum/gas pressure, and the pressure drop, ΔP , was measured as a function of the volume flow rate, U . From these measurements the resistance coefficients, Λ , of the porous media were calculated according to:

$$\Lambda = \frac{d^2 \phi^3 (\Delta P/L)}{\eta v (1 - \phi)^2}, \quad (1)$$

where η is the fluid viscosity and v is the superficial flow velocity (defined by U /cross-sectional area of porous media).

The Reynolds number for porous media flow is defined as:

$$Re = \frac{\rho v d}{\eta (1 - \phi)} \quad (2)$$

where ρ is the fluid density. The Ergun equation then states that for Newtonian fluids:

$$\Lambda = A + B.Re. \quad (3)$$

For low values of Re ($Re < 1$), the resistance coefficient is dominated by the constant term, A . This is the Darcian flow

regime in which the pressure drop increases linearly with the flow rate. At higher Reynolds numbers inertial effects become important and the $B.Re$ term in Eq. 3 becomes appreciable. The values of A and B for Newtonian liquids are found to vary in the literature. McDonald et al. (1979) suggested values of 180 and 1.8, respectively, after extensive analysis of published data, although both A and B are found to vary within around $\pm 15\%$ due to the precise nature of the packing and the roughness of the particles. According to the numerical computations of Zick and Homsy (1982), the values of A should be approximately 157 and 141 for the SC and BCC porous media, respectively.

For greater ease of comparison between the three porous media we have also made estimates of the specific viscosities of the polymer solutions, η_{sp} , by comparison of the resistance coefficient of the solution, $\Lambda_{solution}$, with that of the solvent, $\Lambda_{solvent}$, at equal flow rates, i.e.:

$$\eta_{sp} = \frac{\Lambda_{solution} - \Lambda_{solvent}}{\Lambda_{solvent}}. \quad (4)$$

η_{sp} is plotted as a function of the strain rate based on the superficial flow velocity, $\dot{\epsilon}_{sup}$, which we define geometrically as:

$$\dot{\epsilon}_{sup} \approx \frac{v}{d}. \quad (5)$$

This method has some important advantages over other approaches. Since the flow is unlikely to be strictly creeping flow, i.e. since the Reynolds number will be greater than zero, corrections ought to be made to both $\Lambda_{solution}$ and $\Lambda_{solvent}$ due to inertial forces. However, since the inertial force contributions to $\Lambda_{solution}$ and $\Lambda_{solvent}$ should be essentially equal, the process of subtraction in Eq. 4 should largely obviate any errors due to these effects. Also, since only deviations from Newtonian behaviour appear in the specific viscosity and the pressure drop, data from the three porous arrays can be compared for a given polymer solution.

The HPAA sample used in this study was ALCO-FLOOD 1175A, supplied by Allied Colloids Inc, Suffolk, VA. The molecular weight was very high (nominally $M_w=18 \times 10^6$, with $M_w/M_n \approx 2$), and the degree of hydrolysis was between 0.35 and 0.4. Due to its very high molecular weight the HPAA sample being used was found to be very susceptible to mechanical degradation by the stirring apparatus during preparation of the solutions. For this reason great care was taken to ensure that all of the solutions were prepared in an identical way so that, even if degradation could not be completely avoided, it would have a similar impact upon each solution.

Solutions were prepared at polymer concentrations of $0.001\% \leq c \leq 0.008\%$. The monovalent salt used was NaCl in concentrations between 1 mM and 0.5 M. Analytical grade CaCl_2 , supplied by Riedel-de Haen, Seelze,

Germany, was also used in concentrations between 0.1 mM and 0.1 M.

The solutions were prepared in Pyrex beakers containing 3l of deionised water of pH 6 ± 0.5 . Since Muller and Saez (1999) have shown that the properties of polyelectrolyte solutions can be affected by the order of dissolution of salt and polymer, the required amount of salt was always dissolved in the water first. When the salt had completely dissolved, a vortex was created in the brine using a magnetic stirrer and the required amount of HPAA powder was added. After a few seconds, when the polymer powder had dispersed in the brine, the stirring was reduced to the minimum speed for the following 24 h while the polymer dissolved. Before experimentation the solutions were left to stand without stirring for 30 min. The temperature of the solutions, measured prior to experimentation, was $22 \pm 1^\circ\text{C}$. None of the solutions showed any sign of gel formation or variation in refractive index, and no precipitation of polymer or salt was ever observed.

Results

Crystallographic arrays

Plots of the resistance coefficient, Λ , as a function of Reynolds number, Re , for pure water in the SC and BCC flow cells are shown in Fig. 1. The data points corresponding to both flow cells are well described by the Ergun equation. The Ergun coefficients of Λ for water in the BCC cell are close to the values suggested by McDonald et al. (1979) and Zick and Homsy (1982). However, the Ergun coefficients for water in the SC cell are considerably greater than expected. A similar discrepancy was found between the resistance coefficients recorded for pure DOP through SC and BCC porous media (Haward and Odell, 2003) and also for Newtonian flow through SC and orthorhombic porous media (Haas and Durst, 1982).

Figure 2a,b shows the resistance coefficient as a function of Re for 0.004% solutions of $M_w=18 \times 10^6$ HPAA in

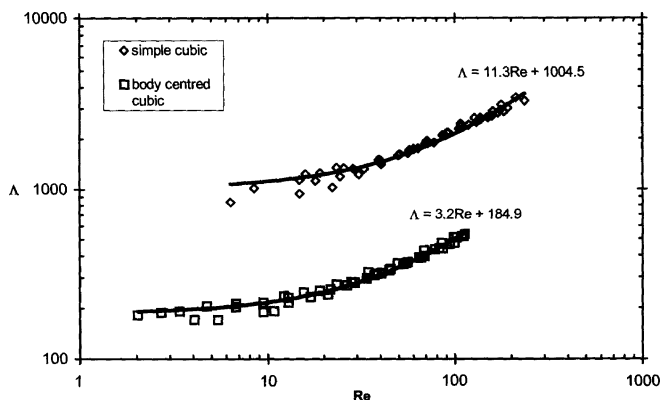


Fig. 1 Resistance coefficient as a function of Reynolds number for pure water in the regularly packed porous media flow cells

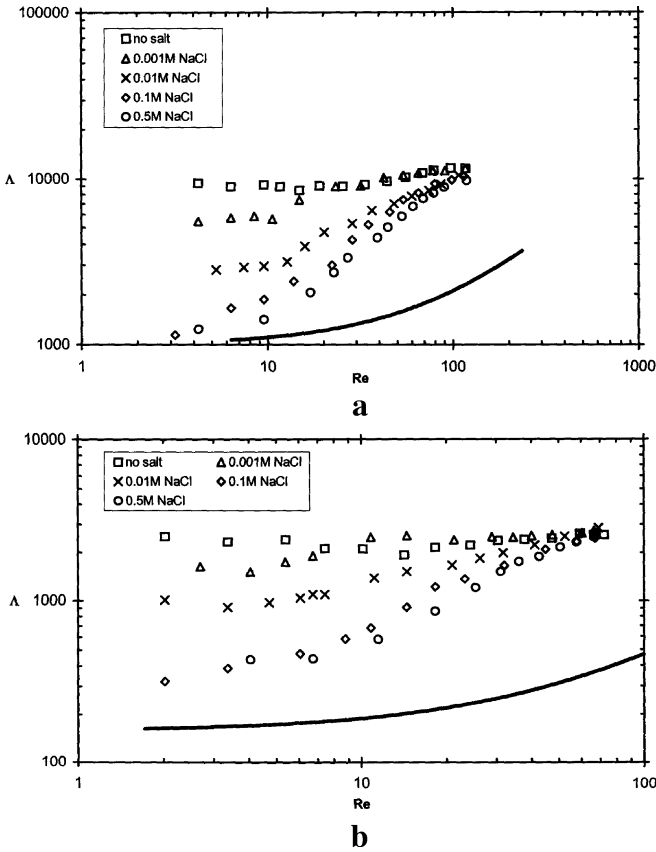


Fig. 2 Resistance coefficient as a function of Reynolds number for 0.004% aqueous solutions of $M_w=18 \times 10^6$ HPAAs in the presence of various concentrations of NaCl in **a** the simple cubic porous media and **b** the body-centred cubic porous media. The solid lines represent linear fits to the data for pure water

various aqueous NaCl solutions in the SC and BCC flow cells, respectively. With no salt present in the solution the resistance coefficient is seen to have a high value for all Re . With increasing salt concentration the value of A at low Re becomes progressively lower, tending towards the Newtonian value. At high salt concentrations (≥ 0.1 M, at which the effect of the salt has essentially saturated) we see behaviour typical of flexible polymers in porous media flow. That is, pseudo-Newtonian behaviour below a critical or onset Reynolds number, Re_o , followed by a non-Newtonian increase in A above Re_o . With increasing Re , the resistance coefficients for the solutions containing NaCl rise to plateau values approximately equal to the value of A for the solution of HPAAs in deionised water. This behaviour with increasing NaCl concentration is similar to the finding of Durst et al. (1981) and is explained by screening of the like negative charges on the polymer backbone. In the absence of salt the polymer molecules are highly expanded at equilibrium, giving the solution a high shear viscosity and reducing the degree of conformational change that can occur in an extensional flow. Molecules display essentially rigid rod-type behaviour and simply

align themselves with the flow axis, which occurs at very low Re . As NaCl is added to the solution, screening of the negative charges on the polymer molecules occurs due to the presence of Na^+ counter-ions. This results in the contraction of the polymer coils, which causes a reduction in the shear viscosity of the solution and results in more flexible polymer molecules.

Figure 3a,b shows the specific viscosity, η_{sp} , as a function of superficial strain rate, $\dot{\epsilon}_{sup}$, derived from the data of Fig. 2a,b, respectively. In this form, significantly more information can be obtained from the data, and subtle differences between the behaviour in the two porous arrays become apparent.

With no NaCl present in the solution, Fig. 3a,b shows that shear thinning dominates the behaviour right through the strain rate range in both flow cells. As the NaCl concentration is increased the shear viscosity becomes reduced and the solutions begin to show a non-Newtonian increase in the apparent specific viscosity above a critical strain rate, $\dot{\epsilon}_c$. The increase in specific viscosity corresponds to the increase in resistance coefficient shown in

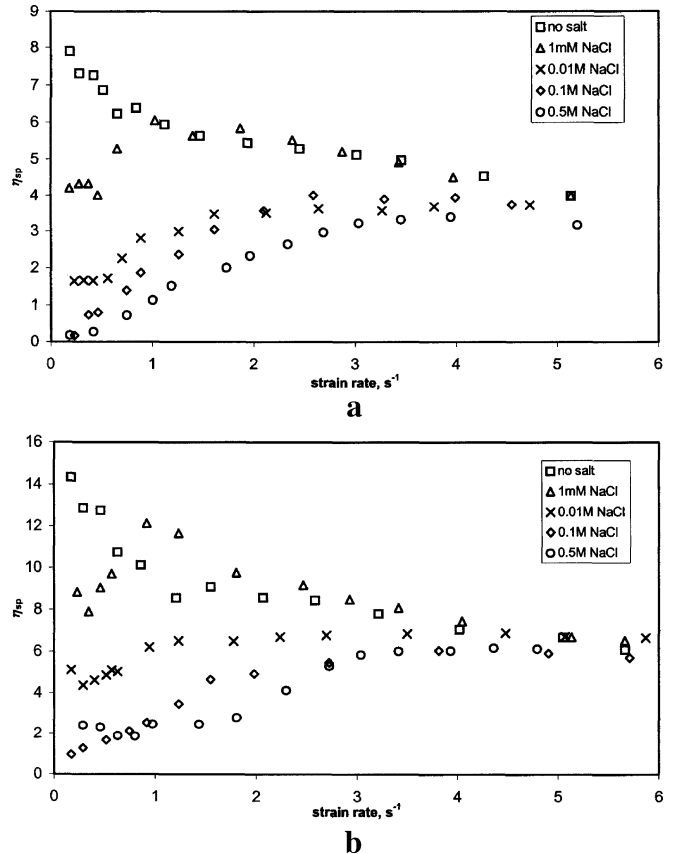


Fig. 3 Specific viscosity as a function of superficial strain rate for 0.004% aqueous solutions of $M_w=18 \times 10^6$ HPAAs in the presence of various concentrations of NaCl in **a** the simple cubic porous media and **b** the body-centred cubic porous media. Derived from Fig. 2a,b, respectively

Fig. 2a,b. In each particular porous medium, the limiting value of η_{sp} at high strain rate has an approximately constant value regardless of NaCl concentration. This suggests that with increasing strain rate, the initially coiled HPAA molecules in the presence of NaCl adopt a conformation similar to that of HPAA in deionised water, i.e. extended. It is striking that the magnitude of the viscosity increase is significantly greater in the BCC array than in the SC array, which is entirely contrary to the behaviour observed by Haward and Odell (2003) using the same porous media flow cells but with solutions of aPS in DOP.

Figure 4a,b show the effect of polymer concentration on the specific viscosity curves for HPAA solutions containing 0.5 M NaCl in the SC and BCC porous media, respectively. The solutions display a non-Newtonian viscosity increase above $\dot{\epsilon}_{sup}$, which scales fairly linearly with polymer concentration, and the effect is discernible even at $c=0.002\%$. For a given solution the critical strain rate is similar in both porous media. However it is consistently observed that the specific viscosity reaches a higher value in the BCC cell than in the SC array.

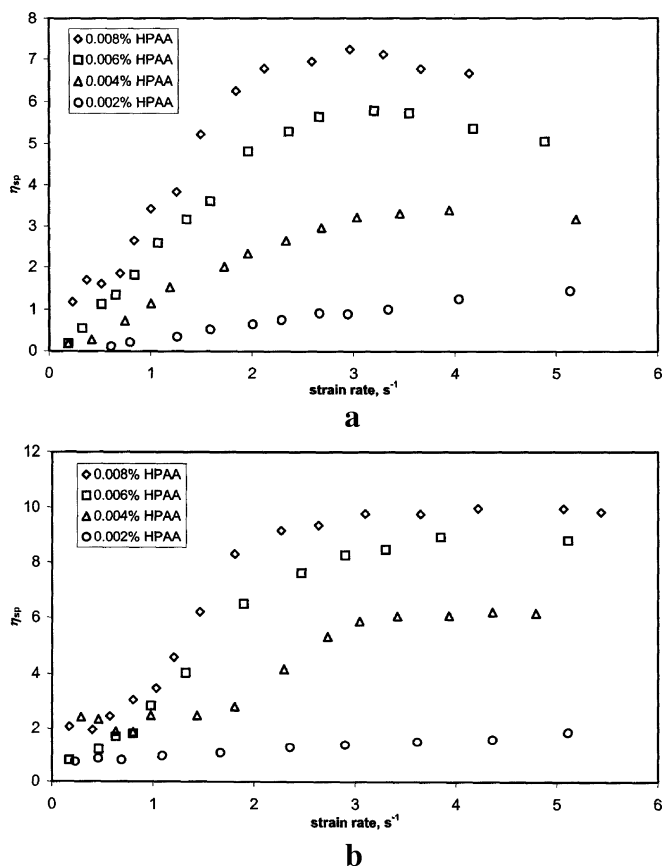


Fig. 4 Specific viscosity as a function of superficial strain rate for aqueous solutions of various concentration of $M_w=18 \times 10^6$ HPAA in the presence 0.5 M NaCl in **a** the simple cubic porous media and **b** the body-centred cubic porous media

The effects of a divalent salt (CaCl_2) on the behaviour of a 0.004% HPAA solution in the SC and BCC porous media are shown in Fig. 5a,b, respectively. Comparison of these figures with Fig. 4a,b, respectively, shows that in general terms, the effect of CaCl_2 is similar to the effect of NaCl. However it is seen that, for a given NaCl concentration, a similar (or greater) reduction in the shear viscosity can be achieved with the addition of a much lower molar concentration of CaCl_2 . In broad terms approximately ten times less CaCl_2 is required to produce a similar effect on the shear viscosity as a given molar concentration of NaCl. Another difference between the effects of NaCl and CaCl_2 on the HPAA solutions is that the plateau values of η_{sp} are significantly reduced with increasing CaCl_2 concentration, which was not so evident with increasing NaCl concentration. The CaCl_2 also causes the onset of non-Newtonian thickening to be delayed to higher strain rates than the monovalent salt. These effects can be explained by the increased screening power of the divalent cation, compared to the monovalent cation, and by the possibility of intramolecular bridging taking place, which could significantly affect the flexibility of the polymer molecules.

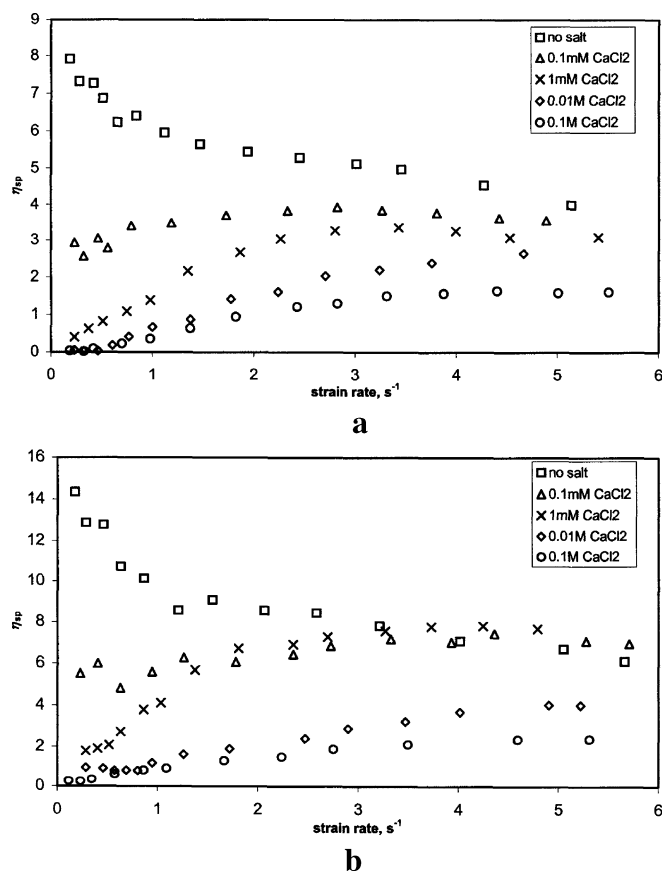


Fig. 5 Specific viscosity as a function of superficial strain rate for 0.004% aqueous solutions of $M_w=18 \times 10^6$ HPAA in the presence various concentrations of CaCl_2 in **a** the simple cubic porous media and **b** the body-centred cubic porous media

Degradation

The performance of polymer solutions used for viscosity enhancement purposes is limited mainly by mechanically and/or thermally induced scission of the polymer chains in flow. There is therefore a great practical interest in experimental results into the degradation of polymer solutions in porous media flow and in understanding the underlying mechanisms behind chain scission.

Accordingly, a short study into the degradation of the HPAAsolutions in the regularly packed porous media was carried out. Initially fresh HPAAsolutions were repeatedly tested in each of the flow cells, and the specific viscosity was measured as a function of strain rate for each successive test run.

Figure 6 shows the results of repeated tests of a 0.004% solution of HPAAsolutions in deionised water in the SC array. It is observed over the course of six experiments that little or no degradation of the polymer occurred.

With 0.5 M of NaCl in the solution, the rate of degradation in the SC array is observed to increase significantly (Fig. 7a). There is a reduction in the peak value of η_{sp} of ~20% between tests 1 and 6. The rate of degradation is observed to be even greater in the BCC array: ~50% reduction in η_{sp} between tests 1 and 6.

The degradation rate is found to increase further when 0.1 M CaCl₂ is added to the solution (Fig. 8). Here a reduction in the peak value of η_{sp} of ~45% is observed in the SC array.

The finding that degradation increases with the addition of salts to the solutions is in agreement with the results of Noik et al. (1995), who performed a similar study with HPAAsolutions in the presence of Na⁺ and Ca²⁺ counterions in a randomly packed porous medium. Noik et al. (1995) explained this finding by the change in molecular conformation due to the counter-ions and, in the case of Ca²⁺, by the possibility of interactions between the HPAAsolutions molecules.

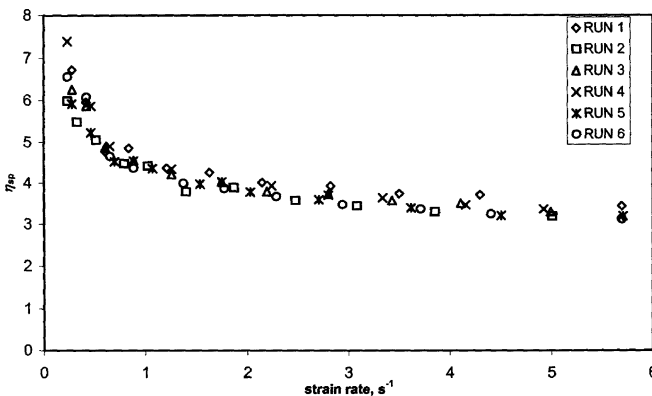
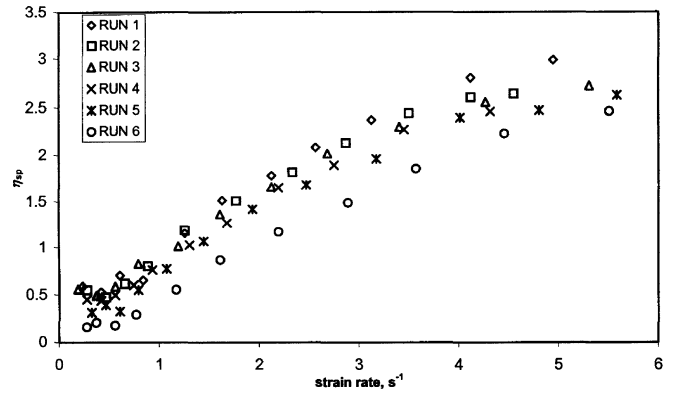
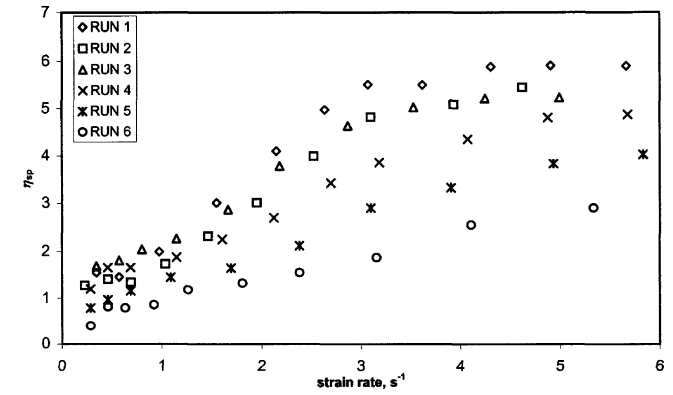


Fig. 6 Degradation of a 0.004% solution of $M_w=18 \times 10^6$ HPAAsolutions in deionised water over repeated test runs through the simple cubic porous media



a



b

Fig. 7 Degradation of 0.004% aqueous solutions of $M_w=18 \times 10^6$ HPAAsolutions in the presence of 0.5 M NaCl in a the simple cubic porous media and b the body-centred cubic porous media

Random array

Figure 9a shows the resistance coefficient, Λ , as a function of Re for 0.004% solutions of HPAAsolutions in the presence of various concentrations of NaCl. The resistance coefficient

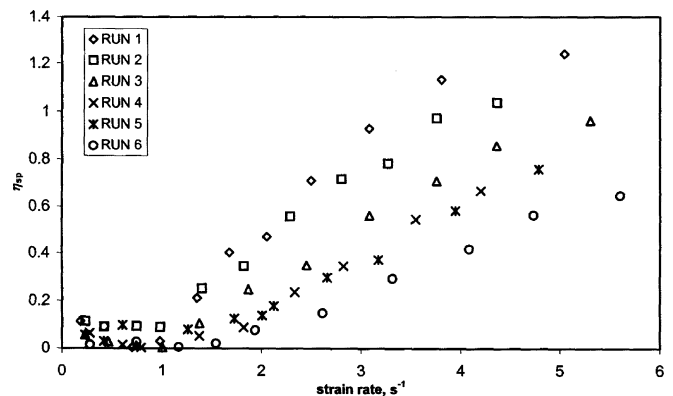


Fig. 8 Degradation of a 0.004% aqueous solution of $M_w=18 \times 10^6$ HPAAsolutions in the presence of 0.5 M CaCl₂ in the simple cubic porous media

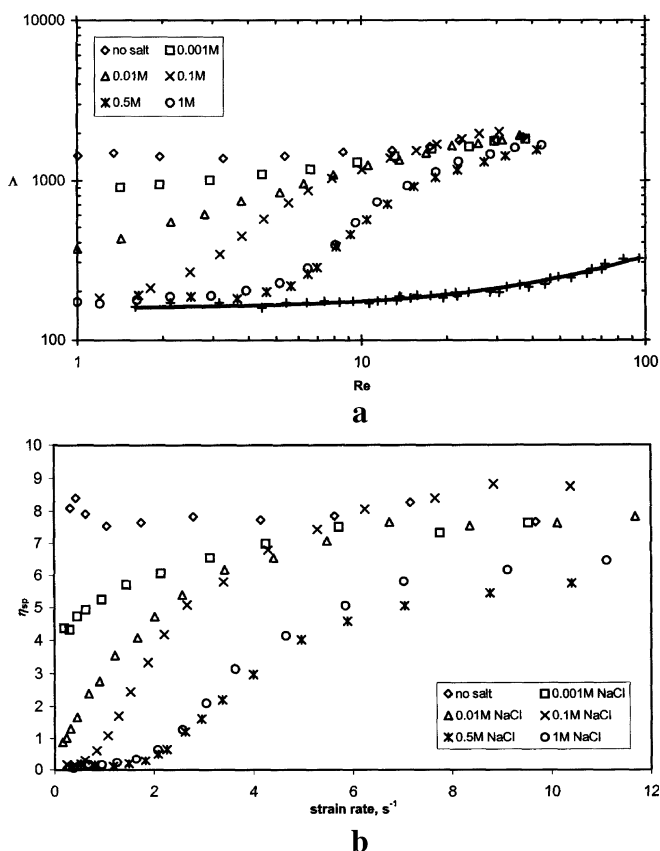


Fig. 9 **a** Resistance coefficient as a function of Reynolds number for 0.004% aqueous solutions of $M_w=18 \times 10^6$ HPAA in the presence of various concentrations of NaCl in the randomly packed porous media. The solid line represents a linear fit to the data points for pure water. **b** Specific viscosity as a function of superficial strain rate derived from the data of Fig. 9a

of water is also shown on the graph and is fitted by the Ergun equation with $A=156$ and $B=1.71$, i.e. $A=156+1.71Re$. These values of A and B agree with the values suggested by McDonald et al. (1979).

The behaviour of the HPAA solutions in Fig. 9a is, qualitatively speaking, very similar to that seen in both of the regularly packed porous media (see Fig. 2a,b). With no salt present the solution shows a resistance coefficient approximately an order of magnitude greater than the solvent. With increasing Re the resistance coefficient remains more or less constant. As the NaCl concentration is increased the resistance coefficient at low Re becomes progressively reduced towards the Newtonian value, and the solution begins to show the characteristic, non-Newtonian increase in flow resistance associated with porous media flows of flexible polymers.

Figure 9b shows the specific viscosity as a function of strain rate for the same solutions as Fig. 9a. The general behaviour of the solutions in Fig. 9b can again be compared to that observed in the regularly packed porous media (see Fig. 3a,b). The curve for the solution not containing salt

shows shear thinning at low strain rate followed by a more or less constant viscosity extending to high strain rates. The shear thinning behaviour is immediately lost on addition of 1 mM of NaCl, and the solution begins to show viscosity enhancement above $\dot{\epsilon}_c$. The effect of the salt has reached a maximum at 0.5 M concentration, by which time the specific viscosity curve shows all the dilatant features typical in extensional flows of flexible polymer solutions. The difference between the curves for 0.5 and 1 M NaCl is within the expected range of experimental error, indicating that the salt has saturated the polymer with positive ions in the 0.5 M solution.

Figure 10 shows the effect of polymer concentration on aqueous solutions of HPAA in the presence of 0.1 M NaCl. It can be seen that the plateau in specific viscosity of the solution increases almost perfectly linearly with HPAA concentration, suggesting that the solutions were dilute and non-interacting. Also a significant non-Newtonian viscosity increase can be observed at a polymer concentration as low as 0.001%.

The behaviour of 0.004% HPAA solutions in the presence of the divalent salt $CaCl_2$ is shown in Fig. 11. As observed in the regular porous media the divalent salts at low concentration have a similar, although stronger, effect on the specific viscosity to NaCl. Broadly speaking, a divalent salt appears to have a similar effect on the shear viscosity of the solution to NaCl with an order of magnitude greater concentration. The differences between the effects of NaCl and $CaCl_2$ in the random porous medium are also consistent with the observations made in the regular porous media (see above). With increasing concentration the $CaCl_2$ is also found to significantly reduce the plateau value of the specific viscosity, as observed in the regular porous media. The $CaCl_2$ also causes the onset of non-Newtonian thickening to be delayed to higher strain rates than the monovalent salt.

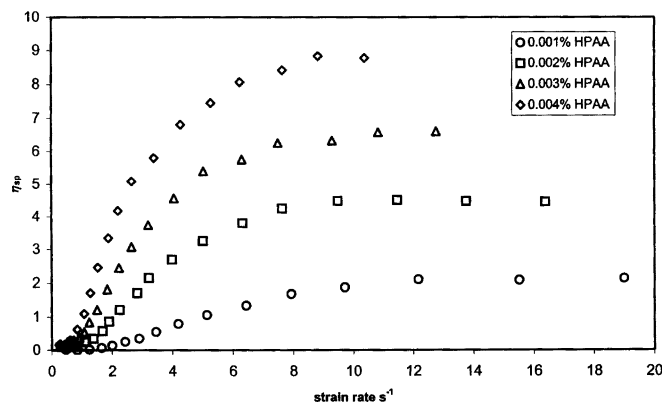


Fig. 10 Specific viscosity as a function of superficial strain rate for 0.004% aqueous solutions of $M_w=18 \times 10^6$ HPAA in the presence of 0.1M NaCl in the randomly packed porous media

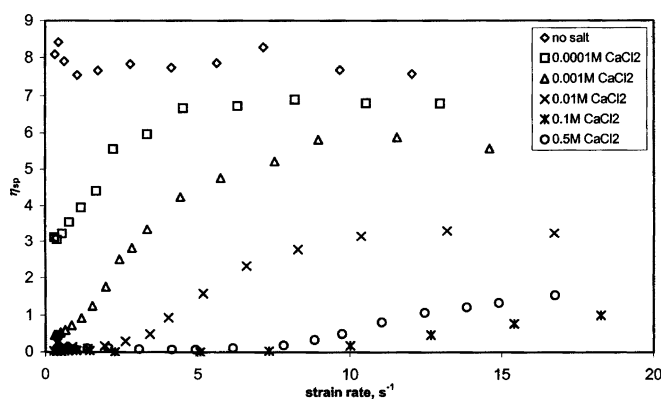


Fig. 11 Specific viscosity as a function of superficial strain rate for 0.004% aqueous solutions of $M_w=18 \times 10^6$ HPAA in the presence of various concentrations of CaCl_2 in the randomly packed porous media

Discussion

With the HPAA solutions a greater specific viscosity was observed in the BCC array than in the SC array: the exact opposite of the finding in the aPS/DOP solutions (Haward and Odell 2003). This may be explained by the different draining characteristics of the polymer molecules. The Mark–Houwink exponent, a , for poly(acrylamide) in water has been shown by various authors to have a value of ~ 0.8 (Scholtan 1954; Klein and Conrad 1980). In the presence of high concentrations of salt the charges on the HPAA backbone are screened and the polymer could be expected to behave as a neutral poly(acrylamide) molecule would in water. This behaviour has been demonstrated by Muller et al. (1979). With the above considerations we should expect the HPAA molecule to be highly expanded, even when its negative charges are effectively screened. This means that the HPAA molecule will have free draining characteristics in comparison to a polymer contained in a theta solvent, such as aPS in DOP. Upon stretching, free draining molecules are not expected to show significant hysteresis in the molecular relaxation time, as the difference between the hydrodynamic interactions in the extended and relaxed states is relatively small. In this case, contractions and expansions in the pore-space would not be effective in extending the polymer molecules since the strain accumulated in a contraction would be entirely lost as the molecule entered the subsequent expansion. Stagnation points in the flow may then become the dominant factor in introducing an extensional component into the flow field.

The results of the flow degradation experiments in the HPAA solutions are consistent with there being a greater degree of polymer extension in the BCC porous medium since a greater rate of mechanical degradation is found in this flow cell. This indicates that in the BCC array, either molecules generally become more highly extended or a greater proportion of molecules become extended (or both).

The results of the flow degradation experiments can be discussed further in terms of the thermally activated barrier to scission (or TABS) theory. The TABS theory is based on the assumption that bond scission occurs when thermal fluctuations overcome the energy barrier for bond dissociation. The role of elongational flow-induced stress in the chain is to reduce this energy barrier from its equilibrium value, therefore increasing the probability of degradation occurring (Odell et al. 1988b).

If a fully extended polymer chain is treated as a pseudocylinder comprised of spherical beads, it can be shown that the maximum stress occurs in the centre of the chain (see Odell and Taylor 1994). This stress is approximately given by $F_c = 0.1 \dot{\epsilon} l_{\max}^2 \eta_0$, where $\dot{\epsilon}$ is the strain rate, l_{\max} is the contour length and η_0 is the solvent viscosity. This is consistent with the experimental finding from a series of stagnation point extensional flow experiments with aPS solutions that the critical strain rate for chain scission depends on the inverse-square of the polymer molecular weight (Odell and Keller 1986).

The highest strain rates achieved in the present degradation experiments ($\dot{\epsilon} \sim 6 \text{ s}^{-1}$) would therefore produce a stress of the order of 10^{-13} N in the centre of the HPAA chain. A similar calculation based on the results of Odell and Keller (1986) suggests that a stress of the order of 1 nN is required to fracture the central covalent C–C bond in the aPS molecule. Although it is apparent that the strain rates calculated for porous media flow are anomalously low, it would seem that a very low activation energy is required for scission of the HPAA molecule and, in addition, that the activation energy is further reduced by the addition of salts to the solution. These opinions are supported by the results of Muller (1981), who observed high rates of degradation in static HPAA solutions in the presence of Na^+ and Ca^{2+} even at modest temperatures (60°C).

Degradation of the HPAA solutions in the randomly packed porous media was not studied; however, since the random porous media possesses stagnation points, degradation should be expected to occur at a rate comparable to that in the BCC porous media. Also it should be considered that in the random array, the fluid passes through many more cycles of strain rate than in the BCC array due to the increased length of the flow cell and the reduced particle size. Therefore it is speculated that a high rate of mechanical HPAA degradation may have been occurring during experimentation in the random porous media, particularly in salt solutions. It should be realised that this may have affected the experimental results from the random porous media, although unfortunately, this is unquantifiable.

Where comparisons can be made, the results from the randomly packed porous medium are qualitatively similar to the results obtained from the regularly packed porous media.

In the randomly packed porous medium the 0.004% solution of HPAA in deionised water (Fig. 9) showed a

resistance coefficient an order of magnitude greater than the Newtonian value, as observed in both of the regular porous media (Fig. 2). With the addition of NaCl the changes in the behaviour of the solution in the random porous medium are also very similar to the changes seen in the regular porous media. As the concentration of NaCl is increased the resistance coefficient at low Re tends to the Newtonian value (in all three flow cells) and the solutions begin to show the characteristic non-Newtonian increase in resistance coefficient associated with porous media flow of flexible polymers. The Reynolds numbers over which non-Newtonian effects occur are also very comparable in all three porous media. The only clear discrepancy between the results is that the resistance coefficient in the SC regular porous medium (Fig. 2a) is significantly greater than in either the BCC or the random porous media (Figs. 2b and 9a, respectively). This may simply be due to non-uniformity in the flow through the SC array.

The plots of specific viscosity as a function of strain rate for 0.004% solutions of HPAA in the randomly packed porous medium (Fig. 9b) are also comparable to the data obtained from the regularly packed porous media (see Fig. 3).

In deionised water the solutions display shear thinning behaviour in all three porous media. However, with increasing strain rate, the shear thinning in the randomly packed porous medium ends quite abruptly at a relatively low strain rate, after which the specific viscosity levels to a constant value. In the regular arrays, on the other hand, the shear thinning appears to continue, decreasingly, through the whole of the strain rate range.

With increasing concentration of NaCl, the solutions in the randomly packed porous medium show a reduction in specific viscosity at low strain rates, as observed in the regular porous media. Also the solutions show an increase in the specific viscosity above a critical strain rate that tends to a plateau value at high strain rates (also observed in the regular porous media). An interesting observation is that, at low strain rates, the specific viscosity curves for the randomly packed porous medium most closely resemble the results from the SC porous medium (Fig. 3a), while at high strain rates, the specific viscosity tends to a plateau value close to that found in the BCC porous medium (Fig. 3b).

For 0.004% HPAA solutions with added CaCl_2 , behaviour in the randomly packed porous medium (Fig. 11) is also very similar to behaviour in the regularly packed porous media (Fig. 5). As before, the specific viscosity in the random porous medium seems to most closely approximate the behaviour in the SC array for low strain rates. At high strain rates the behaviour in the random porous medium tends towards the behaviour in the BCC array. This combination of the behaviour shown in the regular arrays may be rationalized if the random array is

thought of as a random arrangement of regular unit cells, as suggested by Haas and Durst (1982). At low strain rate the shear component of the flow in the random porous media may be most closely approximated by the SC array. At high strain rate the extensional components in the flow may be better approximated by the BCC array due to the presence of stagnation points.

Conclusions

In contrast to our previously published work with solutions of aPS in DOP we have found that above a critical flow rate, dilute aqueous solutions of HPAA display greater increases in specific viscosity in porous media containing trailing stagnation points (i.e. the BCC array) than in porous media devoid of stagnation points (the SC array). We believe that this difference can be explained by the different draining characteristics of the two polymer molecules. In their respective solvents the aPS molecule will have a non-free draining conformation at equilibrium, while the HPAA molecule will be highly expanded and therefore free draining at equilibrium. As such the HPAA molecule will only accumulate limited strain in cyclic flows but can become highly stretched in stagnation point flows with sufficient strain rate. More studies with macromolecules of various equilibrium conformations may help determine the validity of this idea.

We have observed a high rate of mechanical degradation occurring in both the crystallographic porous media, especially in the presence of mono- and divalent salts. We believe this throws doubt on the effectiveness of using such ultra high molecular weight HPAA polymers for oilfield flooding, in particular when brine is to be used as the solvent.

The behaviour of the solutions in the presence of NaCl, compared to the absence of salt, is a clear indicator that the HPAA molecules change from a coiled to an extended conformation above a critical Reynolds number or strain rate. The low concentrations of polymer in the solutions ($0.001\% < c < 0.008\%$) and the lack of significant concentration effects over this range, even in deionised water, suggest that polymer–polymer interactions were not significant in any of the solutions and are therefore not a necessary requirement for the production of a significant viscosity increase in porous media flow. We attribute the non-Newtonian viscosity enhancement to the coil \leftrightarrow stretch transition as envisaged by de Gennes (1974).

Acknowledgments We gratefully acknowledge the support of the EPSRC and EU Aifa Programmes. We thank Prof. AJ Müller for support and helpful discussions.

References

- Dauben DL, Menzie DE (1967) Flow of polymer solutions through porous media. *J Pet Technol* 19:1065–1073
- de Gennes PG (1974) Coil-stretch transition of dilute flexible polymers under ultrahigh velocity gradients. *J Chem Phys* 60:5030–5042
- Durst F, Haas R, Kaczmar BU (1981) Flows of dilute hydrolyzed polyacrylamide solutions in porous media under various solvent conditions. *J Appl Polym Sci* 26:3125–3149
- Haas R, Durst F (1982) Viscoelastic flow of dilute polymer solutions in regularly packed beds. *Rheol Acta* 21:566–571
- Haward SJ, Odell JA (2003) Viscosity enhancement in non-Newtonian flow of dilute polymer solutions through crystallographic porous media. *Rheol Acta* 42:516–526
- Haward SJ, Odell JA (2004) Molecular orientation in non-Newtonian flow of dilute polymer solutions around spheres. *Rheol Acta* 43:350–363
- Hinch EJ (1977) Mechanical models of dilute polymer solutions in strong flows. *Phys Fluids* 20:S22–S30
- James DF, McLaren DR (1975) The laminar flow of dilute polymer solutions through porous media. *J Fluid Mech* 70:733–752
- Klein J, Conrad K (1980) Characterisation of poly(acrylamide) in solution. *Macromol Chem* 181:227–240
- Kulicke WM, Haas R (1984) Flow behaviour of dilute polyacrylamide solutions through porous media. 1. Influence of chain length, concentration, and thermodynamic quality of the solvent. *Ind Eng Chem Fundam* 23:308–315
- Marshall RJ, Metzner AB (1967) Flow of viscoelastic fluids through porous media. *Ind Eng Chem Fundam* 6:393–400
- McDonald IG, El-Sayed MS, Mow K, Dullien FAL (1979) Flow through porous media—the Ergun equation revised. *Ind Eng Chem Fundam* 18:199–205
- Muller AJ, Saez AE (1999) In: Nguyen TQ, Kausch HH (eds) *Flexible chain dynamics in elongational flows: theory and experiment*. Springer, Berlin Heidelberg New York, Berlin
- Muller G (1981) Thermal stability of high-molecular-weight polyacrylamide aqueous solutions. *Polym Bull* 5:31–37
- Muller G, Laine JP, Fenyo JC (1979) High-molecular-weight hydrolyzed polyacrylamides. I. Characterization. Effect of salts on the conformational properties. *J Polym Sci Polym Chem Ed* 17:659–672
- Noik CH, Delaplace PH, Muller G (1995) Physico-chemical characteristics of polyacrylamide solutions after mechanical degradation through a porous medium. *Proc Int Symp Oilfield Chem* 93–100
- Odell JA, Keller A (1986) Flow-induced chain fracture of isolated linear macromolecules in solution. *J Polym Sci Polym Phys Ed* 24:1889
- Odell JA, Taylor MA (1994) Dynamics and thermomechanical stability of DNA in solution. *Biopolymers* 34:1483
- Odell JA, Muller AJ, Keller A (1988a) Non-Newtonian behaviour of hydrolysed polyacrylamide in strong elongational flows: a transient network approach. *Polymer* 29:1179–1190
- Odell JA, Keller A, Rabin Y (1988b) Flow-induced scission of isolated macromolecules. *J Chem Phys* 88:4022
- Saez AE, Muller AJ, Odell JA (1994) Flow of monodisperse polystyrene solutions through porous media. *Colloid Polym Sci* 272:1224–1233
- Scholtan W (1954) Molecular dimensions of polyacrylamide. *Makromol Chem* 14:169
- Zick AA, Homsy GM (1982) Stokes flow through periodic arrays of spheres. *J Fluid Mech* 115:13–26