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The influence of the extensional viscosity of very low concentrations of high molecular mass water-soluble polymers on atomisation and droplet impact.

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Abstract

Background

Water soluble polymers are commonly added to herbicide and pesticide formulations at very low concentrations (100-1000ppm) in order to control the spray characteristics, notably to reduce spray drift and influence droplet bounce.^{1,2} The incorporation of polymeric adjuvants improves the efficacy of the spray solutions, thus enabling crop growers to maximise the performance of agrochemical sprays at lower dose rates of active ingredient. It is important to establish a fundamental understanding of how polymers influence the processes involved in droplet deposition.

Results

The shear and extensional viscosities of a series of high molecular weight, M_w , polyacrylamides ($M_w \sim 10^6 - 10^7$) have been determined at very low concentrations (100 – 1000ppm). The polymer solutions demonstrated typical shear thinning characteristics under shear and strain hardening behaviour under extension above a critical strain rate. The presence of the polymers was shown to increase the size of droplets produced in atomization using an agricultural spray nozzle as measured by laser diffraction. This was attributed to the increase in the extensional viscosity at the strain rates generated under pressure in the spray nozzle and was a function of both polymer concentration and M_w . In addition the presence of polymer was found to have a significant influence on droplet bounce.

Conclusions

The presence of very low concentrations of high molecular weight polyacrylamides significantly influences the size of droplets formed on atomisation and subsequent bounce characteristics. Large extensional viscosities generated above a critical strain rate are responsible for both processes.

Keywords: Polymers; Solutions; Rheology; Drop; Bounce; Spray drift

Introduction

Water soluble polymers are commonly added to herbicide and pesticide formulations at very low concentrations (100-1000ppm) in order to control the spray characteristics, notably to reduce spray drift and in addition to influence droplet bounce and run off.^{1,2} The use of polymers improves the accuracy of deposition and efficacy of the spray solutions, thus enabling farmers to maximise the performance of agrochemical sprays at lower dose rates of active ingredient. This not only reduces costs but also maximises crop yield and benefits the environment. Studies have been reported investigating the atomisation, droplet bounce and retention stages individually, however, as far as we are aware there are none that deal with all of these aspects. There is evidence that polymers that can reduce spray drift can increase droplet bounce and run off and hence reduce the overall efficiency. It is important, therefore, that we gain a fundamental understanding of all of the processes involved in droplet deposition.

During atomisation of agrochemical formulations the role of the polymer is to minimise the proportion of droplets produced below a critical size and hence reduce spray drift.^{3,4} Many studies have been performed to determine the important parameters responsible. It has been demonstrated that there is no simple relationship between surface tension and zero shear

rate viscosity with spray cloud characteristics.⁵ A number of studies have concluded that the polymer acts by increasing the extensional viscosity of the solution.^{1,4,6-8} It has been found that, for random coil polymers, the extensional viscosity of solutions increases above a critical strain rate, due to induced stretching of the polymer chains.⁹⁻¹¹ It has been proposed that in very dilute solution the 'coil-stretch' transition $\dot{\epsilon}$ (c-s) should scale with the molecular mass according to the relationship $\dot{\epsilon}$ (c-s) $\sim M^{(1-\nu)}$ where ν is the Flory exponent which has values of 0.6 and 0.5 in good and θ solvents, respectively. Chain scission may also occur at high extensional strain rates - $\dot{\epsilon}$ (sciss) - and will scale according to the relationship, $\dot{\epsilon}$ (sciss.) $\sim M^{-2\nu}$.¹²⁻¹⁵ Harrison *et al.*¹⁵ investigated the effect of polymer chain rigidity on extensional viscosity. They demonstrated that poly(acrylamide), which is highly flexible, exhibited strain thickening at strain rates of 20s^{-1} . This effect was not observed for carboxymethyl cellulose or xanthan gum, which are much stiffer molecules.

Ferguson *et al.*⁷ investigated the influence of polymers [poly(ethylene oxide), poly(vinylpyrrolidone) and poly(vinyl alcohol)] of varying molecular mass and concentration on spray droplet size. It was found that moderately high molecular mass polymers could give rise to a four-fold increase in the mean droplet diameter. It was concluded that extensional viscosity plays a critical role in the spraying process and in controlling fluid break-up. More recently, Christanti and Walker⁶ studied the jet break up of a series of polymer solutions during atomisation and concluded that strain hardening is the key rheological parameter and that the critical extensional strain rate determines the final spray characteristics. They calculated extensional strain rates during final filament break up from measurements of the filament radius as a function of time. The values were of the same order of magnitude as the critical extensional strain rates obtained from extensional

viscosity measurements performed using a Rheometrics RFX opposed-jet rheometer. Zhu *et al.*¹ studied the influence of a number of high molecular mass polymers - including poly(ethylene oxide)s, non-ionic and anionic poly(acrylamide) copolymers and xanthan gum on spray droplet size. The solutions all had similar equilibrium surface tension values (>60 mNm⁻¹) and the results showed a good correlation between extensional viscosity and droplet size. The work also demonstrated that the polymers lost their effectiveness after recirculation through agricultural sprayers owing to chain scission. Mansour and Chigier¹⁶ found that viscoelastic polymer solutions were more difficult to atomise than inelastic liquids and concluded that the large normal stresses developed by the more elastic polymer solutions was the main reason for the difference in behaviour.

The impact and retraction of droplets onto surfaces has been the subject of numerous theoretical and experimental studies.^{2,17-23} Most studies have been undertaken on Newtonian solutions. Scheller and Bousfield¹⁸ have developed a model to account for inertial, viscous and surface tension forces on maximum spread radius and Mao *et al.*²⁰ have proposed a model that predicts the tendency to rebound as a function of maximum spread and static contact angle. It has recently been demonstrated by high speed photography that droplet rebound can be inhibited by the presence of small amounts of a flexible polymer.^{2,22} Experiments revealed similar impact and expansion stages for pure water and dilute polymer solutions, but the retraction stage was very different. For pure water the drops retracted violently and part of the drop ejected from the surface. For the dilute polymer solutions droplet retraction was much slower and the drop remained at the surface.

The aim of the present work is to investigate the influence of extensional viscosity on the atomisation of very dilute aqueous solutions (~100ppm) of a range of high molar mass polyacrylamides of varying molecular characteristics and their subsequent deposition onto

hydrophobic surfaces. A novel aspect of this publication is the use of capillary break-up studies to examine the strain hardening behaviour of the polymer solutions thus providing a high strain extensional viscosity - which is clearly more suitable than a low strain extensional viscosity for comparison to high strain processes such as spray atomization.

Materials

The study included a range of non-ionic, anionic and cationic polyacrylamide derivatives (supplied by CIBA Specialty Chemicals, Bradford). Anionic PAM derivatives consisted of poly(acrylamide (AAm)-co-acrylic acid (AA) of the structure $-(\text{CH}_2\text{CHCONH}_2)_x-(\text{CH}_2\text{CHCO}_2\text{H})_y-$ where x and y are the percentages of acrylamide and acrylic acid respectively. Cationic PAM derivatives consisted of poly(acrylamide-co-dimethylaminoethyl methacrylate (quaternised)) of the structure $-(\text{CH}_2\text{CHCONH}_2)_x-(\text{CH}_2\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3)_z-$ where z is the percentage of DMAEMA. The molecular mass distributions of all of the polymers were determined by asymmetric flow field-flow fractionation (AsFFFF) coupled to multi-angle laser light scattering (MALLS) and refractive index (RI) detection.

The weight average molecular mass, M_w , and number average molecular mass, M_n , obtained are summarised in Table 1. All of the samples are polydisperse as noted by the M_w / M_n ratios.

Methods

Shear viscosity

The shear viscosity of dilute polymer solutions was determined using a TA Instruments 2000 controlled stress rheometer equipped with a 60mm (or 40mm) stainless steel 2° cone and plate geometry and water trap to prevent evaporation and sample drying. All tests were conducted at $25 \pm 0.1^\circ\text{C}$.

Extensional viscosity

The extensional viscosity of the samples was determined at 25°C using a capillary break-up extensional rheometer (*CaBER*) produced by Thermo Haake. The rheometer operates by the formation of an unstable fluid filament which is allowed to relax and undergo break-up governed by its own dynamics. In a capillary break-up experiment, a symmetrical cylinder or bridge of fluid is formed between two spherical plates of predetermined diameter. The plates undergo rapid separation to a predetermined distance thereby applying a uniaxial extensional strain to the sample. The resulting decay of the filament mid-point diameter, denoted D_{mid} , is monitored with respect to time, t , using a laser micrometer. The filament undergoes relaxation and decay governed by the viscous, elastic and surface tension forces acting within the fluid. The surface tension, σ , of the fluid must be known in order to calculate an apparent extensional viscosity, η_E , according to the following relationship²⁴;

$$\eta_E = \frac{-\sigma}{dD_{mid}/dt} \quad [2]$$

Both Newtonian and viscoelastic fluids are characterised by a critical break-up time, t_{crit} , dependent upon the fluid properties. After stretching, a Newtonian fluid undergoes viscocapillary drainage until the point of rupture is reached.²⁵ For a Newtonian fluid, the filament diameter is expected to decay linearly with time and undergo rapid break-up. The

apparent extensional viscosity for a Newtonian fluid should be constant over the imposed range of strains. The stretching of polymer chains within a viscoelastic fluid can give rise to strain hardening.¹⁰ The decay response of a viscoelastic fluid when exposed to uni-axial extension is dominated by the formation of a thin axi-symmetrical fluid filament which decays exponentially with time, characterised by a constant relaxation time. This relaxation time relates to a timescale for the stretching of polymer molecules in extensional flows leading to an increase in extensional viscosity.²⁶⁻²⁸ In a viscoelastic fluid, elastic stresses within the thread resist capillary pressure and prevent the filament from breaking.²⁸⁻²⁹ Fluids which display a viscoelastic response when studied by capillary break-up typically exhibit small regions of Newtonian behaviour at short and long timescales in addition to the exponential decay response. Sharply accelerated filament break-up gives rise to the latter Newtonian regime and is linked to the finite extensibility of polymer chains resulting in a high constant extensional viscosity attained at high strain rates.^{26,30-31}

Cylindrical plates of diameter 4mm were employed separated by an initial gap of 2mm giving rise to an aspect ratio of 0.5. Samples were loaded between the plates using a needle attached to a 1mL syringe so that a visually symmetrical cylinder of fluid was formed.

Both the shear and extensional rheometry measurements were performed on solutions comprised of polymer in a 95:5 glycerol:water solvent mixture. This high viscosity solvent was utilized in order to obtain measurements at very low polymer concentrations, typical for those used during atomisation experiments (~100ppm).

Atomisation and determination of droplet size

A pressure rated water filter cartridge (Liff model NP1) was modified to feed a 110° flat fan agricultural spray nozzle (Lurmark F110/0-6/3) and was used to generate a spray of aqueous

droplets. A Malvern Instruments Spraytec RS particle sizer (670nm) equipped with a 450mm lens (capable of detecting particles in the 2.25-850 micron size range) was employed to measure the droplet size of the spray produced. The height and distance of the spray head from the receiver lens was controlled and maintained at 30cm and 15cm respectively. Time history analysis showed little variation in particle size with time therefore flash mode measurements were utilised with a data acquisition rate of 500Hz over a test of duration 15,000ms. Average particle size distributions are automatically calculated by the Spraytec software utilising the multiple scattering correction. The results were expressed in terms of the surface - volume mean diameter, $D[3,2]$. The droplet size was shown to be a function of pressure. For example for water the droplet size was 318nm, 102nm and 88 nm respectively at pressures of 1, 2 and 3 bar. Values did not change significantly above 3bar and were very reproducible hence this pressure was used for all the experiments.

Spray drift

The % spray drift was determined by mass balance. Solutions were sprayed into a wind tunnel of length 3m, height 2m and width 2.5m. A spray head containing a 110° flat fan nozzle was mounted 60cm above the floor. Wind at 6mph (measured at the centre of the tunnel) was generated using a fan placed at a distance of 10cm behind the nozzle. A 2.5m by 3m collection device was positioned centrally under the spray head such that a 2.8m length of the collection device was down wind to the nozzle. The solution to be tested was placed in a brass spray canister attached to the spray head. The canister, tubing and spray head were then weighed. A source of compressed air was used to expel the test solution through the nozzle at a pressure of 3bar onto a pre-weighed plastic sheet, which was used to cover the collection area. The test solution was sprayed for 135s. The canister and spray head were

then reweighed in order to determine the weight of the solution expelled. The plastic sheet was carefully folded and reweighed. The mass of the solution collected was then calculated and used to determine the loss of spray due to drift.

Droplet bounce

A method was developed to monitor the impact of droplets onto a surface. Droplets of approximately 1000 μm were produced using a purpose built piezoelectric generator fitted with a 500 μm glass nozzle. Water sensitive paper was used to confirm that a reproducible droplet size was obtained. Droplets were allowed to fall a set distance onto the surface of a leaf (pea) inclined at an angle of 45°. The distance that each drop bounced was measured. Results reported are the average for 10 drops onto three replicate leaves taken from different plants.

Results and discussion

Shear and extensional viscosity

Viscosity - shear rate profiles for polymer 30A in 95:5 glycerol:water are shown at varying concentrations in Figure 1. The sample shows typical pseudoplastic behaviour with a tendency towards a Newtonian plateau at low shear rates followed by a shear thinning regime at higher shear rates. The low shear viscosity increases with increasing polymer concentration as expected. Similar behaviour is observed for the other polymers (data not shown).

The decay of the filament midpoint diameter with respect to time, determined on the capillary break-up rheometer is shown in Figure 2 for polymer 30A at varying

concentrations. A Newtonian response is observed at long times close to break-up and the critical break-up time is observed to increase with increasing polymer concentration. This accelerated filament decay which correlates with the maximum stretching of polymer chains results in a constant high strain apparent extensional viscosity.

The following equation was used to fit the data (shown as solid lines in Figure 2) ^{25,28,32};

$$R_{mid}(t) = R_1 - \frac{(2X-1)\sigma}{6\eta_E}t \quad [3]$$

where R_{mid} is the midpoint filament radius, R_1 is the initial radius of thread at $t=0$, σ is the surface tension of the fluid, η_E is the extensional viscosity, t is the time and $X = 0.7127$ for inertia-less viscous fluid filaments and viscous Newtonian fluids with a smooth necked profile. The exponential part of the filament diameter versus time plot (indicated by the dotted lines in Figure 2) can be described by the following equation ²⁶;

$$D_{mid}(t) = D_o \exp\left(\frac{-t}{3\lambda}\right) \quad [4]$$

and is characterised by the longest relaxation time, λ (where D_o is the initial filament diameter).

The extensional viscosities of polymer 30A solutions at varying concentration are given as a function of the Hencky strain and the extensional strain rate in Figure 3a. The strain rate is observed to diverge at a critical time (observed in Figure 3b) associated with polymer chains reaching their limit of finite extensibility. It is noted that the extensional viscosities shown in Figure 3a are significantly greater than the shear viscosities and this is conveniently

illustrated in Figure 4 which plots the Trouton ratios for polymer 30A at a concentration of 100ppm as a function of strain rate.

The extensional viscosities increase with increasing strain rate and a pseudoplateau value is obtained. The plateau value increases with increasing polymer concentration. Similar behaviour is observed for the other polymer solutions (data not shown). The technique does not permit extensional viscosities to be obtained at very low strain rates and hence it was not possible to determine the critical strain rate at which strain hardening occurred. In previous studies on polyacrylamides in a Boger fluid using the Rheometrics RFX extensional rheometer it was shown that the critical strain rate of solutions at a concentration of 830ppm was typically in the range of 0.1 s^{-1} to 1 s^{-1} for samples with a M_w of ~ 1 to 3×10^6 Da and was proportional to $\sim M^2$.¹¹ Interestingly it was noted that the critical strain rate was found to be independent of concentration for solutions below the coil overlap concentration. Dexter⁸ measured the extensional viscosity of a range of very dilute polyacrylamide solutions by passing the solutions through a bed of screens at a series of pressures. This technique avoids the necessity of using Boger fluids. It was noted that high molecular mass ($> 5 \times 10^5$ Da) polyacrylamides and polyacrylamide / acrylic acid copolymers showed marked extensional thickening above a critical flow rate reaching a maximum value which increased with increasing polymer concentration. Significant extensional viscosities were obtained even for polymer concentrations of 10ppm and lower. The critical strain rate was not quoted directly but from their data it is estimated to be of the order of $\sim 10 \text{ s}^{-1}$ for a 250ppm polyacrylamide solution with M_w 1×10^7 Da. The critical strain rate was shown to decrease with increasing polymer M_w but contrary to the work of Pelletier *et al.*¹¹ was also found to vary with polymer concentration.

The high strain plateau extensional viscosities of the various polymer samples in 95:5 glycerol:water at a concentration of 100ppm are plotted as a function of M_w in Figure 5.

Although it appears that there is no correlation between extensional viscosity and M_w for the samples as a whole, it is noted that there is reasonable correlation for each of the classes of polymer, i.e. nonionic, anionic and cationic, with the extensional viscosity increasing with the polymer molecular weight as expected.^{8,11} Since the measurements were performed in a solvent of elevated viscosity compared to aqueous solutions, it is expected that chain expansion due to the presence of charged groups along the polymer backbone would be minimal for the anionic and cationic polymers and it is perhaps surprising that the viscosities for the different polymers do not superimpose on a single line. The reason for this may be due to the polydisperse nature of the samples and / or due to differences in chain flexibility or architecture for the different types.

Atomisation

The droplet sizes of the sprays produced by the various polymers in water at a range of concentrations are reported in Table 2.

The average droplet size obtained for water alone was 88microns. The droplet size increased significantly by the addition of very low concentrations of polymer and was found to increase with increasing polymer concentration. The equilibrium surface tensions were all > 60mN/m and hence small differences in surface tension between samples were not expected to have a significant effect on droplet size (or droplet bounce described below).

The droplet sizes produced by the various aqueous polymer solutions at 100ppm concentration are given as a function of the high strain extensional viscosity (determined in 95:5 glycerol:water) in Figure 6. It is noted that the droplet size increases with increasing high strain plateau extensional viscosity and that the rate of increase is different for the various polyacrylamide types i.e. nonionic, anionic and cationic. Dexter⁸ also demonstrated

an increase in the droplet size with increasing extensional viscosity and argued that the high extensional viscosity of these flexible polymers even at very low concentrations retarded break-up of the fluid sheet produced on atomisation.

The droplet sizes obtained on atomisation are given in Figure 7 as a function of the relaxation times obtained from the extensional viscosity measurements. The droplet size is seen to increase with increasing relaxation time and there appear to be subtle differences between the various polymer types reflecting variations in the flexibility of the polymer chains and their ability to undergo coil stretching.

Spray drift

The number of droplets lost to spray drift increases significantly for droplets below a particular size. For the experiments carried out in our purpose-built wind tunnel we note that the % lost to spray drift increases significantly as the % droplets under 150 microns increases. This is illustrated in Figure 8.

The % lost to spray drift for the varying samples are plotted as a function of extensional viscosity in Figure 9. The results show that spray drift decreases with increasing extensional viscosity as a consequence of the increase in droplet size.

Droplet bounce

The influence of the various polymers at a concentration of 100ppm on droplet bounce was investigated and the results obtained are plotted as a function of apparent extensional viscosity in Figures 10 and as a function of the relaxation time in Figure 11. It is noted that droplet bounce is reduced significantly with increasing high strain extensional viscosity and relaxation time.

When droplets impact onto a surface they undergo radial expansion reaching a maximum diameter and then retract. On retraction the droplet height on the surface increases and above a certain value will lead to a proportion of the drop leaving the surface. The impact velocity is an important factor controlling rebound while the nature of the surface has a relatively minor influence. The retraction rate determines whether or not a drop rebounds off the surface and it has been shown that this process can be markedly suppressed by the presence of high molecular weight polymers.^{2,22} The polymer reduces the rate of retraction, thus reducing the droplet height and hence inhibits droplets bouncing off the surface. High speed photography has shown that the impact and expansion stages occur within ~ 2 ms while the retraction stage is an order of magnitude slower.² Typical extensional strain rates experienced on retraction are expected to be of the order of 10^3 s^{-1} and hence it is the high strain extensional viscosity that is important when considering droplet bounce.

Conclusions

This work has shown that the presence of very low concentrations of high molecular weight polyacrylamides and polyacrylamide copolymers has a significant influence on droplet size formed on atomisation and also on droplet bounce following impact on a surface on aqueous solutions. It has been argued that the large high strain extensional viscosities generated by these materials above a critical strain rate is the key parameter responsible for both processes. There is a good correlation between the extensional viscosity and the relaxation time under extension with both droplet size on atomisation and droplet bounce on impact.

Acknowledgements

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References

1. Zhu H, Dexter RW, Fox RD, Reichard DL, Brazee RD, Ozkan HE, Effects of polymer composition and viscosity on droplet size of recirculated spray solutions. *J Agr Eng Res* **67**:35-45 (1997).
2. Bergeron V, Bonn D, Martin YV, Vovelle L, Controlling droplet deposition with polymer additives. *Nature* **405**:772-774 (2000).
3. Akesson NB, Steinke WE, Yates J, Spray atomization characteristics as a function of pesticide formulations and atomiser design. *J Environ Sci Heal B* **29**:785-814 (1994).
4. Mun RP, Young BW, Boger DV, Atomisation of dilute polymer solutions in agricultural spray nozzles. *J Non-Newt Fluid Mech* **83**:163-178 (1999).
5. Downer RA, Hall FS, Thompson RS, Chapple AC, Temperature effects on atomization by flat-fan nozzles: Implications for drift management and evidence for surfactant concentration gradients. *Atomization Sprays* **8**:241-254 (1998).
6. Christanti Y, Walker LM, Surface tension driven breakup of strain-hardening polymer solutions. *J Non-Newt Fluid Mech* **100**: 9-26 (2001).
7. Ferguson J, Hudson HE, Warren BCH, The break-up of fluids in an extensional flow field. *J Non-Newt Fluid Mech* **44**:37-54. (1992).
8. Dexter RW, Measurement of extensional viscosity of polymer solutions and its effects on atomization from a spray nozzle. *Atomization Sprays* **6**:167-191 (1996).
9. Dontula P, Pasquali M, Scriven LE, Macosko CW, Can extensional viscosity be measured with opposed-nozzle devices. *Rheol Acta* **36**:429-448 (1997).

10. Barnes HA, A Handbook of Elementary Rheology, University of Wales Institute of Non-Newtonian Fluid Mechanics Publishers, Aberystwyth (2000).
11. Pelletier E, Viebke C, Meadows J, Williams PA, Dilute polyacrylamide solutions under uniaxial extensional flow. *Langmuir* **19**:559-565 (2003).
12. DeGennes PG, Coil stretch transition of dilute flexible polymers under ultrahigh velocity gradients. *J Chem Phys* **60**:5030-5042 (1974).
13. Cifre JGH, de la Torre JG, Steady state behaviour of dilute polymers in elongational flow. Dependence of the critical elongational rate on chain length, hydrodynamic interaction, and excluded volume. *J Rheol* **43**:339-358 (1999).
14. Andrews NC, Doufas AK, McHugh AJ, Effect of solvent quality on the rheological and rheoptical properties of flexible polymer solutions. *Macromolecules* **31**:3104-3108 (1998).
15. Harrison GM, Mun R, Cooper G, Boger DV, A note on the effect of polymer rigidity and concentration on spray atomization. *J Non-Newt Fluid Mech* **85**: 93-104 (1999).
16. Mansour A, Chigier NJ, Air-blast atomization of non-Newtonian liquids. *J Non-Newt Fluid Mech* **58**:161-194 (1995).
17. Bennett T, Poulidakos D, Splat quench solidification – estimating the maximum spreading of a droplet impacting a solid surface. *J Mater Sci* **28**: 963-970 (1993).
18. Scheller BL, Bousfield DW, Newtonian drop impact with a solid surface. *AIChE J* **41**: 1357-1367 (1995).
19. Wirth W, Mechanisms controlling leaf retention of agricultural spray solutions. *Pestic Sci* **33**: 411-420 (1991).

20. Mao T, Kuhn DCS, Tran H, Spread and rebound of liquid droplets upon impact on flat surfaces. *AIChE J* **43**:2169-2179 (1997).
21. Crooks R, Boger DV, Influence of fluid elasticity on drops impacting on dry surfaces. *J Rheol* **44**:973-996 (2000).
22. Crooks R, Cooper-White J, Boger DV, The role of dynamic surface tension and elasticity on the dynamics of drop impact. *Chem Eng Sci* **56**:5575-5592 (2001).
23. Zhang XG, Basaran OA Dynamic surface tension effects in impact of a drop with a solid surface. *J Colloid Interface Sci* **187**:166-178 (1997).
24. Oliveira MSN, McKinley GH, Iterated stretching and multiple beads on a string phenomena in dilute solutions of highly extensible flexible polymers. *Phys Fluids* **17**:071704 (2005).
25. McKinley GH, Tripathi A, How to extract the Newtonian viscosity from capillary break-up measurements in a filament rheometer. *J Rheol* **44**:653-670 (2000).
26. Stelter M, Brenn G, Yarin AL, Singh RP, Durst F, Validation and application of a novel elongational device for polymer solutions. *J Rheol* **44**:595-616 (2000).
27. Stelter M, Brenn G, Yarin AL, Singh RP, Durst F, Investigation of the elongational behaviour of polymer solutions by means of an elongational rheometer. *J Rheol* **46**:507-527 (2002).
28. Anna SA, McKinley GH, Nguyen DA, Sridhar T, Muller S, Huang J, James DF, An interlaboratory comparison of measurements from filament-stretching rheometers using common test fluids. *J Rheol* **45**: 83-114 (2001).
29. Tirtadmadja V, Sridhar T, A filament stretching device for measurement of extensional viscosity. *J Rheol* **37**:1081-1102 (1993).

30. Entov VM, Hinch EJ, Effect of a spectrum of relaxation times on the capillary thinning of a filament of elastic liquid. *J Non-Newt Fluid Mech* **72**:31-53 (1997).
31. Bazilevskii AV, Entov VM, Lerner MM, Rozhkov AN, Failure of polymer solution filaments. *Polym Sci Ser A* **39**:316- 324 (1997).
32. Papageorgiou DT, On the breakup of viscous threads. *Phys Fluids* **7**:1529-1544 (1995).

List of Figures

Figure 1. Viscosity shear rate curves for varying concentrations for polymer 30A.

Figure 2. Decay of filament midpoint diameter with time for polymer 30A at varying concentrations. Solid line shows the fit according to equation [3] and the dashed line according to equation [4].

Figure 3a. Extensional viscosity versus Hencky strain for varying concentrations of polymer 30A in a Boger fluid. Solid lines indicate the high strain extensional viscosity plateau.

Figure 3b. Divergence of strain rate with time during the capillary break-up of solutions of polymer 30A in glycerol:water mixture (95:5).

Figure 4. Trouton ratio for polymer 30A at a concentration of 100ppm as a function of strain rate.

Figure 5. High strain extensional viscosity as a function of M_w .

Figure 6. Droplet size, $D[3,2]$ obtained for various polymers at a concentration of 100ppm as a function of the high strain extensional viscosity.

Figure 7. Droplet size, $D [3,2]$ obtained for various polymers at a concentration of 100ppm on atomisation as a function of the polymer relaxation time.

Figure 8. % spray lost to drift as a function of the % of droplets below 150microns.

Figure 9. % spray lost due to drift as a function of apparent extensional viscosity (high strain plateau) for the various polymers at 100ppm.

Figure 10. Droplet bounce as a function of the extensional viscosity (high strain plateau) for the various polymer solutions at 100ppm. Dotted arrow indicates the decrease in bounce observed for solutions that exhibit larger high strain plateau extensional viscosities.

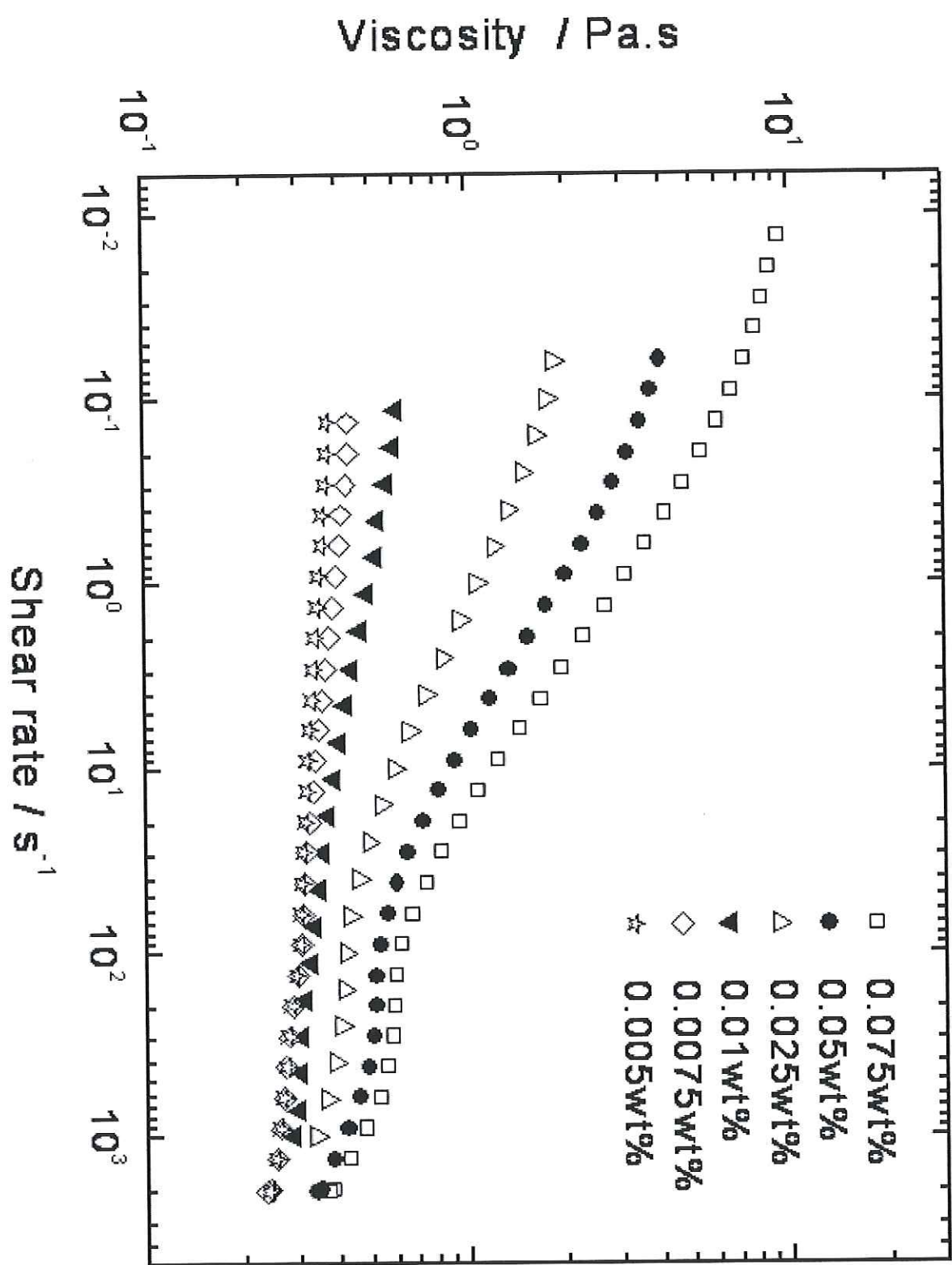
Figure 11. Droplet bounce as a function of the relaxation time for the various polymers at a concentration of 100ppm.

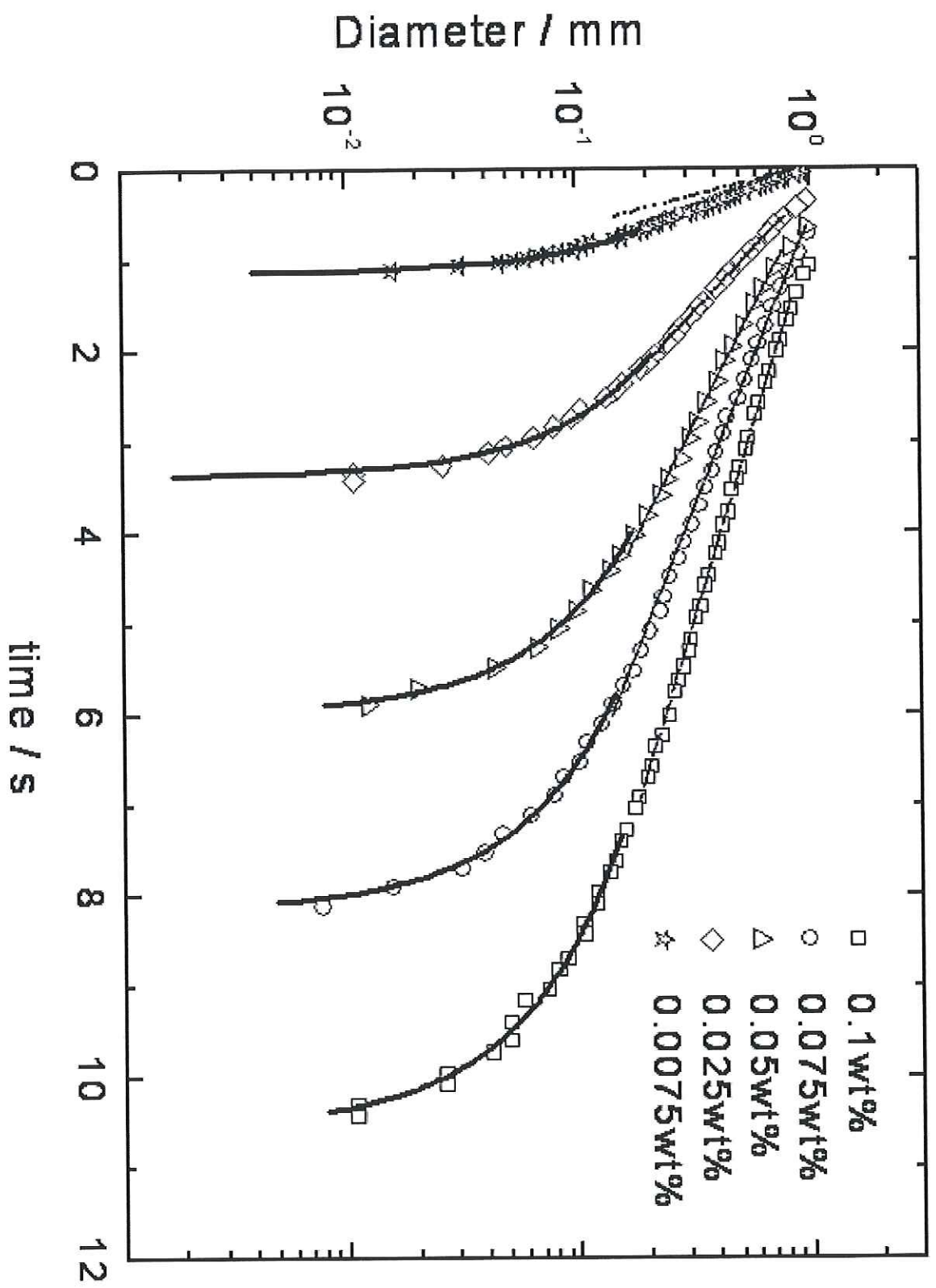
Table 1. Molecular weight characteristics of the various polymers.

	code	M_w Da x 10 ⁶	M_n Da x 10 ⁶	M_w/M_n
Non-ionic PAM 1	N1	2.76	1.77	1.56
Non-ionic PAM 2	N2	0.77	0.58	1.33
96% anionic PAM	96A	15.18	8.84	1.72
70% anionic PAM 1	70A	7.62	6.01	1.27
30% anionic PAM	30A	5.57	4.03	1.38
40% cationic PAM	40C	4.62	3.05	1.52
75% cationic PAM 1	75C1	3.38	1.19	2.84
75% cationic PAM 2	75C2	10.42	3.57	2.92
20% cationic PAM 1	20C1	6.64	5.33	1.24
20% cationic PAM 2	20C2	2.57	2.38	1.08

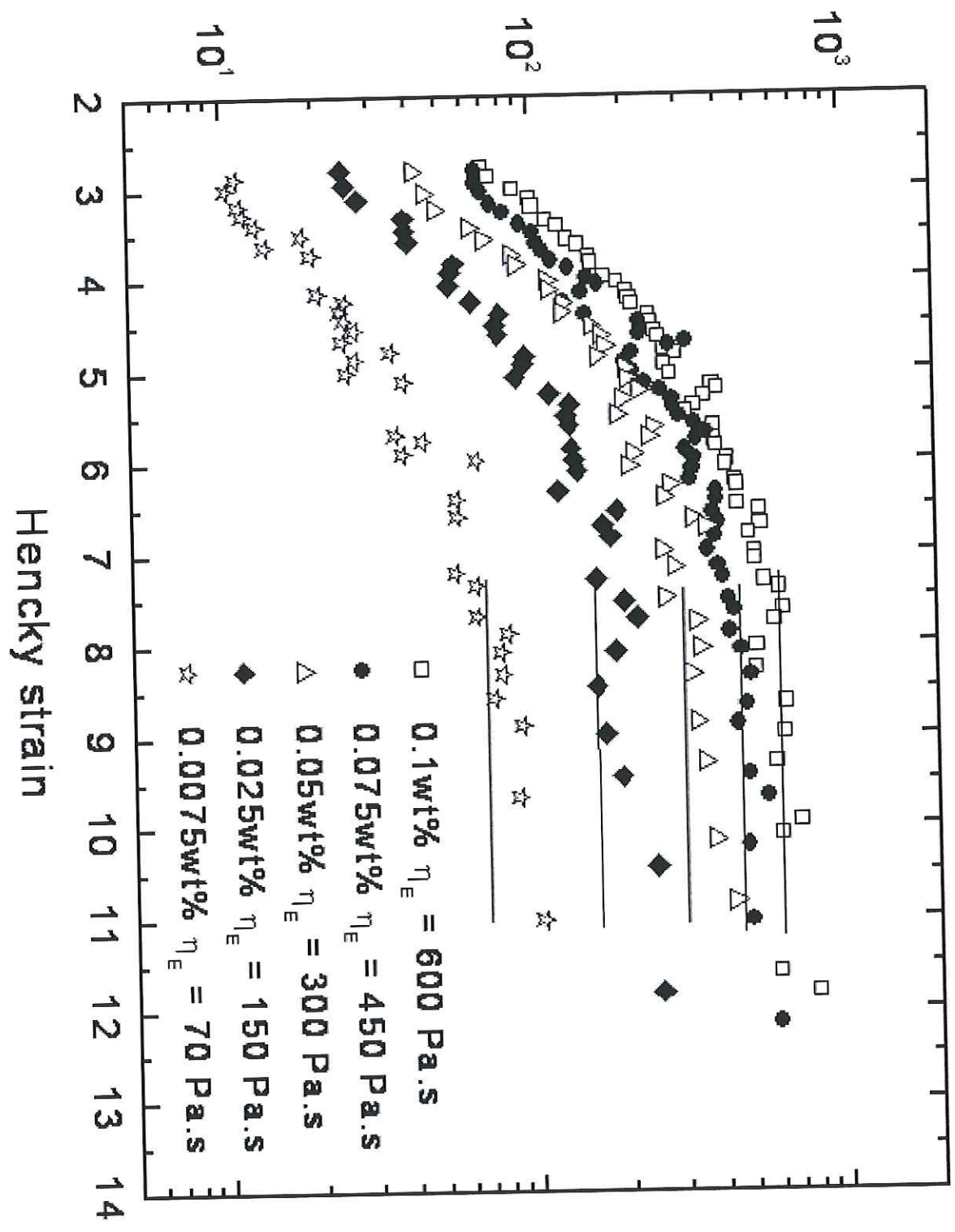
Table 2. Droplet size for solutions of the various polymers at different concentrations.

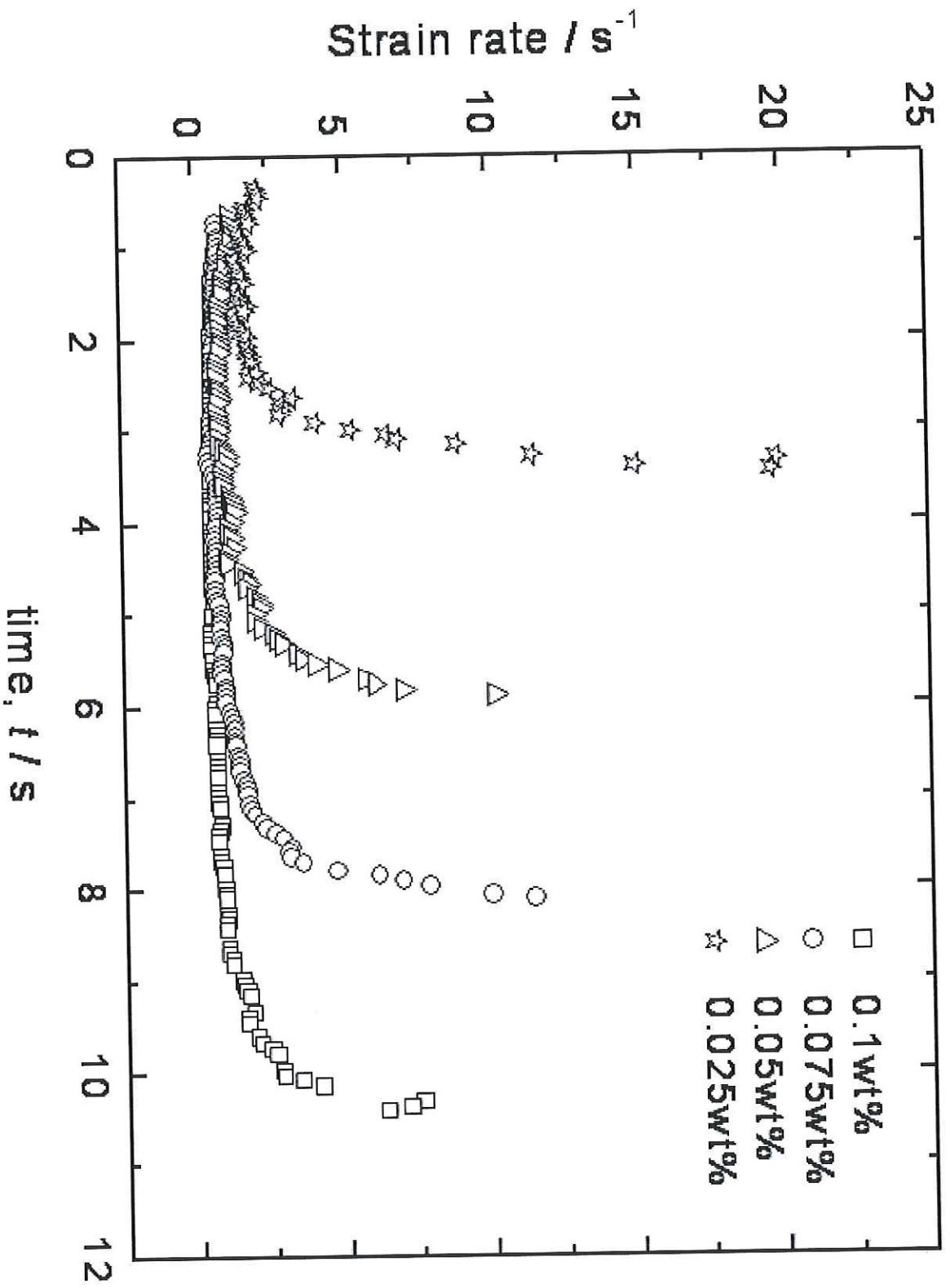
		D[3,2] / nm \pm 2nm			
		50ppm	75ppm	100ppm	250ppm
water	88				
NI		104		120	156(200ppm)
N2		90		88	
96A		99		122	
70A		89		86	
30A		98	100	102	149
40A		105		126	
75C1		104		107	
75C2		101		122	
20C1		115	128	153	666
20C2		99		110	

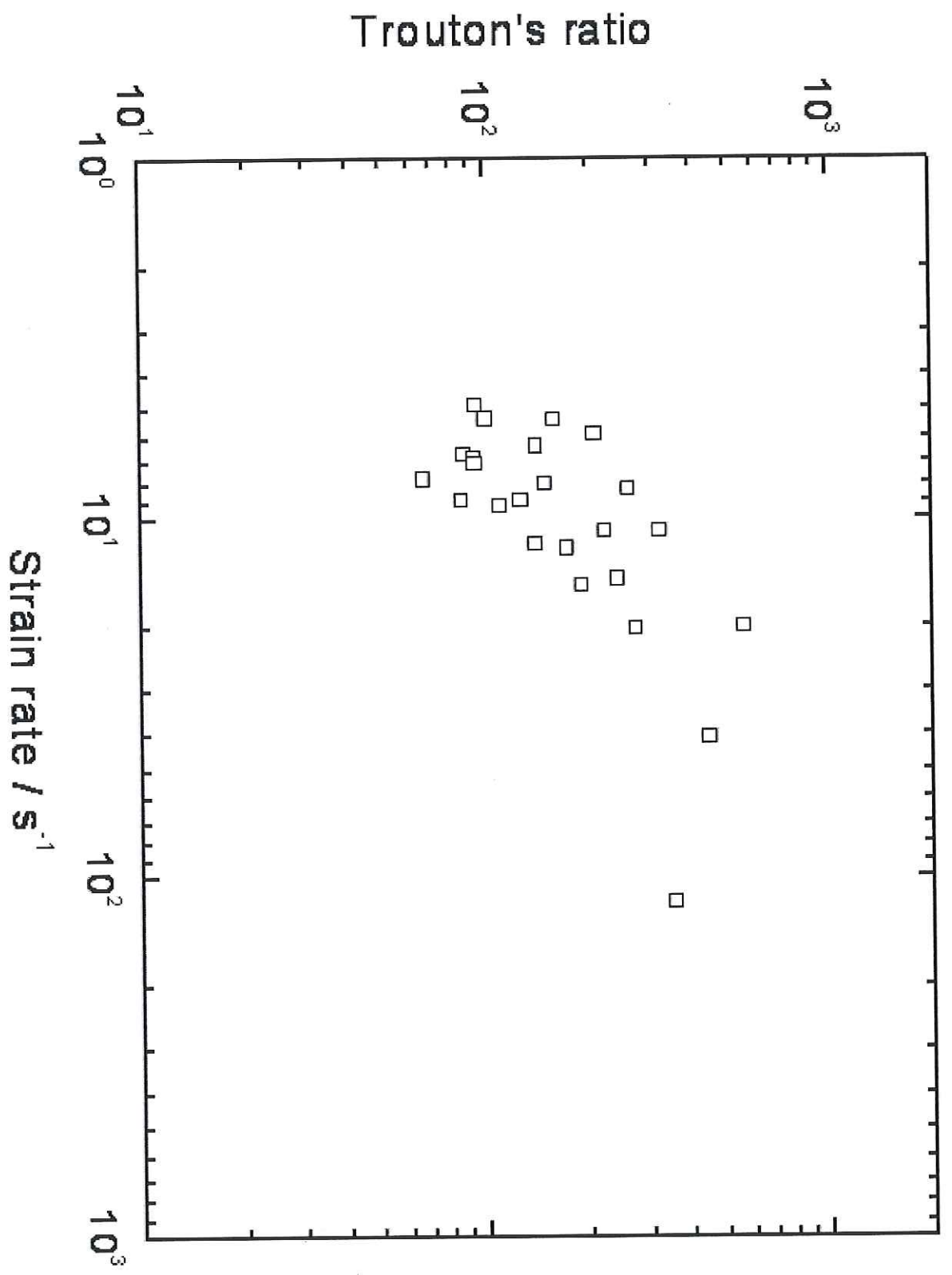


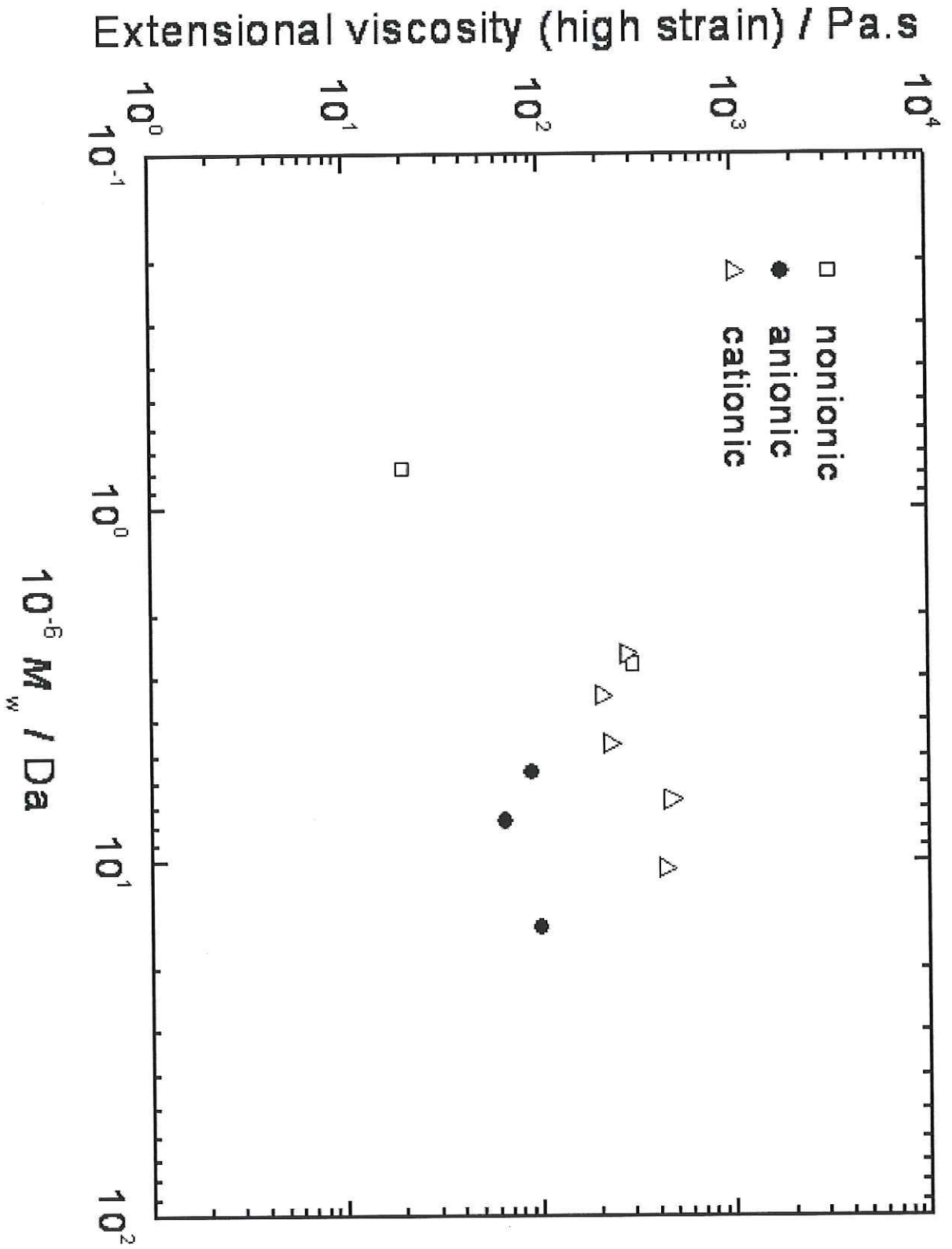


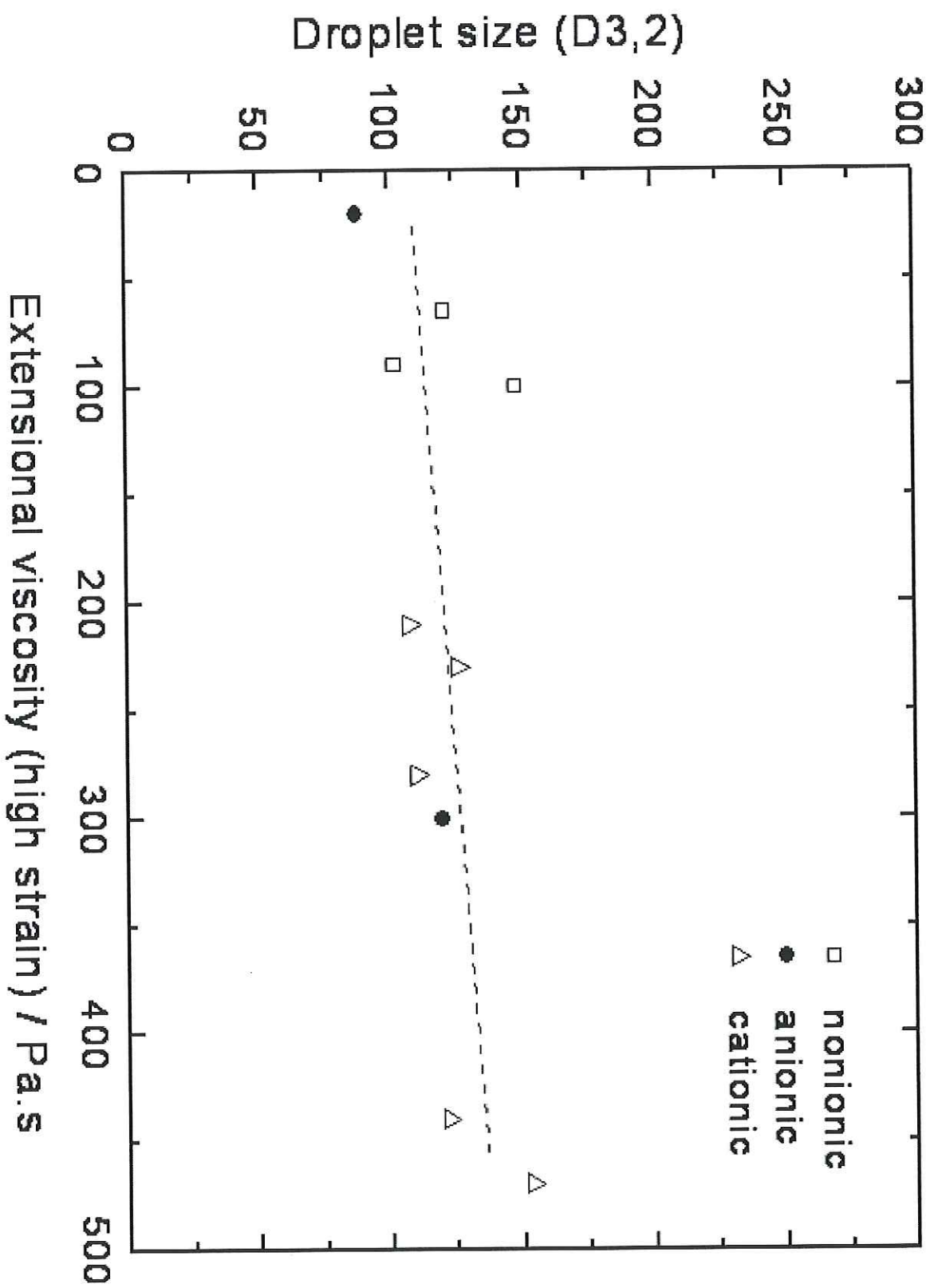
Apparent extensional viscosity / Pa.s











Droplet size (D3,2)

