Flow-Induced Polymer Degradation during Ink-Jet Printing

Khalid A-Alamry^{1}, Keith Nixon^{1}, Rachel Hindley^{1}, Jeffrey A Odell^{2} and Stephen G. Yeates^{1*}
(1) Organic Materials Innovation Centre, School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom
(2) HH Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK.

Abstract

We report for the first evidence of flow-induced polymer degradation during inkjet printing for both poly(methylmethacrylate) and polystyrene in good solvent which has significance for the deposition of functional and biological materials.

Introduction

Ink-jet printing has developed as an important technology for the defined spatial deposition of polymer solutions in applications as diverse as graphics, textiles, digital electronics and displays (1-4) where the polymer may function in the role of dispersant (5), binder (6) or functional material (7). It has long been recognised that the addition of polymer to an ink has a strong impact on the nature of the drop generation and ejection process, with the drop break-up behaviour being in part related to the strain hardening resulting from the presence of polymer passing through a strong elongational flow field (8-12). The microrheological explanation for strain hardening is the sudden transition of the polymer chain from a coiled to a stretched state, which is accompanied by a strong increase in the hydrodynamic drag. The coil-stretch transition occurs for linear polymers at a critical strain rate (ε_{crit}) where the rate of deformation of the chain exceeds its rate of relaxation so that it passes from a slightly distorted random coil to an extended state, This critical condition is achieved when the critical Weissenberg-number ($W_{\varepsilon crit} = \varepsilon_{crit}.\tau_{1}$) > 0.5, where τ_1 denotes the longest relaxation time (13,14). For the inkjet process the strain rate at the nozzle tip is typically greater than 50,000 s^{-1}, and as a consequence the critical Weissenberg-number is exceeded for all polymers having Mw > 50,000 Da at the pinch region, the point at which the ligament is attached to the nozzle tip meniscus (9,10).

Flow induced deformations can also lead to irreversible change in the structure of a complex fluid. The mechanical degradation of polymers in elongational flow fields has long been recognised and can lead to a reduction in average polymer molecular weight (15-17). The passage through an elongational flow field exerts strong hydrodynamic forces upon a coiled polymer molecule in solution as it stretches orients and extends in the direction of flow. If the elongational forces on the molecule are sufficiently strong, and the rate of chain stretching far exceeds the rate of chain relaxation, the polymer backbone can be broken (18).

Here we report the first observation of and conditions for the mechanical degradation of polymer molecular weight under conditions of drop on demand inkjet printing. These observations have implications with respect to the printing of functional and biological materials where retention of polymer composition is critical.

Experimental

Materials

All solvents, linear atactic poly(methyl methacrylate) (PMMA; M_w = 145 – 1630 kDa, polydispersity (PDi) ≤ 1.3 and M_w = 909, PDi = 1.8) and polystyrene (PS; M_w 123 – 2000 kDa, PDi ≤ 1.3 and Mw = 900 kDa, PDi = 1.9) were obtained from Sigma Aldrich UK and used as received. Solutions were prepared by gentle agitation and allowed to stand for 24 hours before use. Prior to inkjet printing samples were filtered through a glass microfibre filter (diameter 47 mm, 0.26 mm thick, 1.2 µm retention and filtration speed of 100/100 ml), after which there was no change in either solution viscosity (+/- 0.1 cP at 25 °C) or determined polymer molecular weight and distribution.

Instrumentation

Ink-jet printing was carried out using both a MicroJet ™ drop-on-demand dispensing device (Microfab, MJ-AB-01) and a Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix, Inc., Santa Clara, USA). The MicroJet ™ dispenser consists of a 50 µm internal diameter glass nozzle with a piezoelectric actuator sleeve driven by an external power supply. A bipolar waveform, with a 3 µs rise time, 40 µs duration and 3 µs decay followed by a 3 µs echo and 3 µs rise, was employed with an external drive frequency and voltage of 4000Hz. and 30 to 60V respectively. To prevent nozzle tip wetting and to create reproducible printing conditions, the glass capillary was regularly cleaned with a 20 wt.-% solution of potassium hydroxide in demineralized water and rigorously flushed with the appropriate jetting solvent. The Dimatix DMP-2800 was fitted with a waveform editor and a drop-watch camera system which allows manipulation of the electronic pulses to the piezo jetting device for optimization of the drop characteristics as it is ejected from the nozzle. The nozzle plate consists of a single raw of 16 nozzles of 23 µm diameter spaced 254 µm with typical drop size of 10 pl and drop diameter 27 µm. All results are the average of at least three runs under each experimental condition.

Results and Discussion

Inkjet Printing of Polymer Solutions

Clear miscible solutions of PMMA in γ-butyrolactone and PS in γ-butyrolactone and tetralin were prepared. Solvents were chosen on the basis that they are classified as good solvents having relative Energy Difference (RED) numbers (19) in the range 0.6 – 0.9. Boiling points are in the range 204 - 208 °C enabling sustained inkjet printing at room temperature without significant nozzle blockage. For each polymer - solvent combination the overlap concentration c* was defined using the classification of Flory (20) for a flexible polymer in solution, c* = 1/[η] and polymer concentration expressed as a reduced concentration [η].c or c/c* (21).

Solutions of PMMA and PS in γ-butyrolactone were prepared at reduced concentration = 0.15, 0.33, 0.5, 0.75, 1.0. For all fluids low shear viscosity and surface tension were in the range 1 – 10 cP and 29 – 40 mN/m at 25 ^{o}C respectively, indicating that they are suitable for inkjet printing $^{(22)}$. Despite this it was not possible to inkjet print all fluids using either the Microfab or Dimatix print head, it being noted that both PMMA and PS showed comparable behaviour at equivalent molecular weight although it should be noted that the maximum reduced concentration evaluated was unity and it is probable that for lower molecular weight polymers the threshold concentration will indeed be higher as previously reported $^{(12)}$. We observe that as molecular weight increases it become increasingly more difficult to jet higher concentration fluids $^{(23)}$.

The longest polymer chain relaxation time is typically described by the Zimm non-free-draining relaxation time, $\lambda z = \eta_s[\eta]M_w/RT$ $^{(1,24)}$; where η_s is the viscosity of the solvent, $[\eta]$ is the intrinsic viscosity of the polymer solution and M_w is the weight average molecular weight. The apparent universality of Zimm behaviour is believed to arise either from the fact that elongational flow experiments only probe the dynamics of the partially stretched coil $^{(25)}$, or that the coil-stretch transition is essentially non-equilibrium since molecules only experience a finite residence time in the flow field $^{(26)}$. Since the critical strain rate (ε_{crit}) for deformation from a slightly distorted random coil to an extended state is exceeded for all polymers studied then strain hardening results in a rapid increase in fluid viscosity. Since maximum relaxation time (λ_z) scales as $M_w^{1.6\text{-}1.7}$ for a random coil polymer in a good solvent then at high molecular weight it can be very long indeed exceeding the time scale for ligament detachment from the nozzle tip meniscus which for the Microfab printhead is between 80 – 90 µs irrespective of applied voltage. The residual viscoelasticity within the ligament therefore resists drop break-up being amplified for very high molecular weight polymer at lower than overlap concentration where resultant chain entanglement of the partially relaxed chains can damp out fully drop break up.

Molecular weight Degradation

For each fluid, drop ejection velocity (v) was determined stroboscopically $^{12)}$, and the strain rate at the nozzle tip (ε) calculated using $\varepsilon = v/D$ where D is the nozzle diameter $^{(24)}$. Molecular weight and distribution for all samples were determined before and after printing. Unless specified otherwise all results are for polymer in γ-butyrolactone with equivalent results being observed in both acetophenone and tetralin.

Fluids were jetted through the Microfab single nozzle glass capillary, 50 µm internal diameter, at 50 V with drop velocity between 2.5 – 5.5 ms^{-1} giving a calculated elongational strain rate at the nozzle tip between 50,000 – 110,000 s^{-1}. All polymers having a PDi ≤ 1.3 showed no change in molecular weight and distribution. However both PMMA 909 kDa, PDi = 1.9 and PS 900 kDa, PDi = 1.8 show reproducible broadening in molecular weight distribution and a shift to lower molecular weight the nature of which is dependant upon the reduced concentration of the fluid, Figure 1.

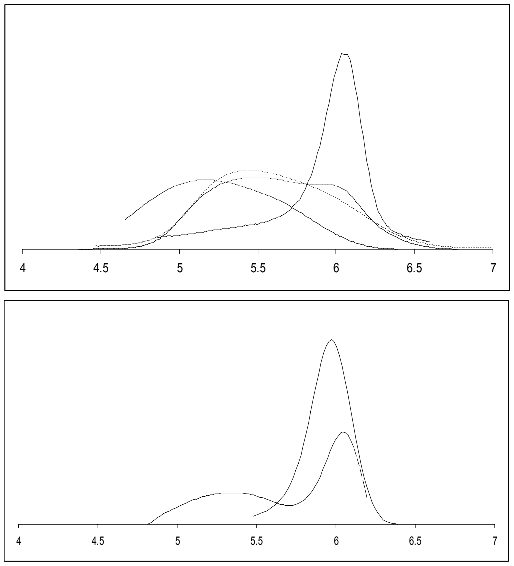
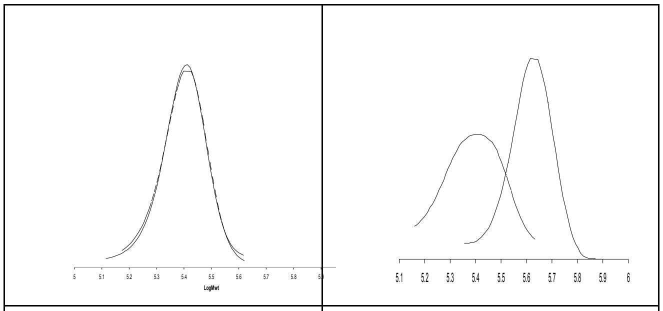


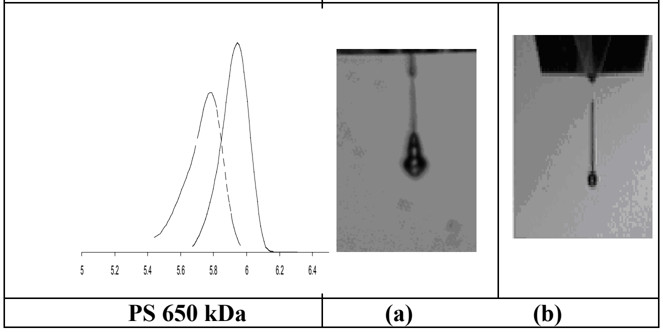
Figure 1: *Effect of reduced concentration on molecular weight distribution (WF/dLogMwt against log mol wt) before and after single pass jetting for PMMA 909 kDa (top) and PS 900 kDa (bottom) in γ-butyrolactone jetted at 50V using a Microfab Printhead at 25 ^{o}C. Before jetting (—). After jetting c/c* = 0.15 (– · –), c/c* = 0.33 (– –), c/c* = 0.5 (— —).*

Molecular weight degradation is more pronounced at low reduced concentration with no degradation being observed at c/c* = 0.5 at 50 V for PS 900 and at c/c* = 0.75 for PMMA 909. It is noted that not all the distribution appears to undergo molecular weight degradation and repetitive jetting of PMMA 909 kDa at c/c* = 0.33 shows no significant reduction in molecular weight although a slight broadening to low molar mass was observed.

For solutions of PMMA in γ-butyrolactone and PS in γ-butyrolactone and tetralin were prepared ink jet printed through a Dimatix DMP-2800 10 pl nozzle, 23 µm internal diameter droplet velocities were between 6.0 – 10.0 ms^{-1}. As a consequence of the smaller nozzle diameter higher elongational strain rates are experienced; 200,000 – 300,000 s^{-1}. Only single pass experiments were performed and for low polydispersity PMMA and PS we observe molecular weight degradation for polymers having M_w = 145 – 590 kDa M_w = 290 – 650 kDa respectively but only for the most dilute solutions, c/c* = 0.15, Figure 2. The highest molecular weight sample tested PMMA 1390 kDa, PDi = 1.16 did not show molecular weight degradation under any of the conditions tried. In all cases the polymer chains break essentially at the middle of the chain leading to an approximate halving of molecular weight. PMMA 909 kDa, PDi = 1.9 and PS 900 kDa, PDi = 1.8 showed reproducible broadening in molecular weight distribution and a shift to lower molecular weight only at c/c* = 0.15, because higher concentrations are at the limit of jet ability.



PS 170 kDa **PS 290 kDa**



PS 650 kDa **(a)** **(b)**

Figure 2: *(WF/dLogMwt against log mol wt) before and after single pass jetting for low polydispersity PS in tetralin at c/c* = 0.15 jetted at 18-26 V using Dimatix 10pl DMP Printhead at 25 °C. Before jetting (—).Single pass jetting (– –). (a) Drop shape in Microfab at drop break off for 650 kDa at c/c* = 0.15 and c/c* = 0.33.*

As previously discussed the mechanical degradation of polymers in elongational flow fields generated by several different geometries has long been recognised and can lead to a reduction in average polymer molecular weight (15-17). Early work on cross-slot devices, which generate an opposing-jets geometry, require a large number of passes through the system to observe chain-scission since only a small percentage of the polymer solution passes through the stagnation point at any one time (15,6,27-29). Conversely transient elongational flows imposed by sudden contractions have been reported to lead to molecular weight degradation of the whole distribution after a single pass, under a continuously applied pressure, for solutions of polyethylene oxide, polyacrylamide and polystyrene in the semi-dilute regime, c/c* = 1.5 – 20 (30-33). Such configurations are characterised by both a high contraction ratio, typically > 35:1, long residence time in a typical elongational flow field of 45,000 s^{-1} giving a Deborah number (De), which is the ratio of the characteristic relaxation time of the polymer solution to the characteristic flow time of the system on the order of 550 (17,34) indicating the polymer chains are being stretched much more rapidly that they can relax.

We can consider the inkjet printhead as a short residence time contraction in that the fluid is forced from the large diameter ink chamber through the nozzle constriction. The Microfab glass capillary represents a constriction ratio on the order of 10:1, whist for the Dimatix head the constriction ratio is unknown but believed to be of the same order of magnitude. Based upon average measured drop velocities the residence time of the fluid in the constriction is short, on the order of 10 μs, after which the fluid begins to relax as the ligament and droplet form. (12)

In the case of low polydispersity polymers we only observe molecular weight degradation at elongational shear rates > 200,000 s^{-1}, for PMMA and PS having M_w = 145 – 590 kDa M_w = 290 – 650 kDa respectively which corresponds to De of the order 4 - 45 but only in the dilute solution regime c/c* = 0.15. From drop visualisation these fluids show characteristic Newtonian behaviour, Figure 2a, outside this range showing behaviour consistent with a viscoelastic fluid, that is stable ligament formation and drop break off at the nozzle tip meniscus, Figure 2b. Within the dilute solution regime the forces required to break the chains are transmitted through viscous energy dissipation due to friction between solvent and polymer molecules. In this regime chain breakage can be induced either by overstretching when the strain rate increases well beyond the critical strain rate (ε_{crit}), that is the stretching rate is high enough to exceed the rate of relaxation or by turbulance (9,10,28), it being shown that in dilute solution only those molecules that are virtually fully stretched can undergo central scission (30).

PMMA 909 kDa, PDi = 1.9, PS 340 PDi = 1.8 and PS 900 kDa, PDi = 1.8 show molecular weight degradation which is printhead (strain rate) and concentration dependant, with reproducible broadening in molecular weight distribution and a shift to lower molecular weight. The results are consistent with almost random scission along the chains inferring that the forces required to break the chain are transmitted either by valence bonds, i.e. network chains and junctions or discrete entanglements rather than by hydrodynamic interaction. Greater broadening is observed at low polymer concentration where we approach the concentration where chain interaction in elongational flow (c+) is not possible (31).

Conclusions

We report the first evidence of flow-induced polymer degradation during inkjet printing for both poly(methylmethacrylate) and polystyrene in good solvent which has significance for the deposition of functional and biological materials. Polymers having weight average molecular weight (M_w) either less than 100 kDa or greater than approximately 1,000 kDa show no evidence of molecular weight degradation. The lower boundary condition is a consequence of low Deborah number imposed by the printhead geometry and the upper boundary condition due to visco-elastic damping. For intermediate molecular weights the effect is greatest at high elongational strain rate at low solution concentration with higher polydispersity polymers being most sensitive to molecular weight degradation. For low polydispersity samples, PDi ≤ 1.3 chain breakage is essentially centro-symmetric induced either by overstretching when the strain rate increases well beyond the critical strain rate, that is the stretching rate is high enough to exceed the rate of relaxation or by turbulence. For higher polydispersity samples, PDi chain breakage is consistent with almost random scission along the chain inferring that the forces required to break the chain are transmitted either by valence bonds, i.e. network chains and junctions or discrete entanglements rather than by hydrodynamic interaction.

Acknowledgements

The authors would like to thank The Saudi Royal Government and the EU 6th Framework Programme Digitex project.

References

1. B.J. de Gens, P.C.Duineveld, U.S.Schubert, Adv. Mater. **2004**, 16, 203.
2. P.Calvert, Chem. Mater. **2001**, 13, 3299.
3. J.F.Dijksman, P.C.Duineveld, M.J.J.Hack, A.Pierik, J.Rensen, J.E. Rubingh, I.Schram, M.M.Vernhout, J. Materials Chem. **2007**, 17(6), 511.
4. M.R Boehmer, R. Schroeders, Jan A.M. Steenbakkers, S.H.P.M.de Winter, P.A Duineveld, J.Lub, W.P.M. Nijssen, J.A.Pikkemaat, H.R.Stapert, Colloids and Surfaces, A: Physicochemical and Engineering Aspects **2006**, 289(1-3), 96.
5. J. Merrington, P. Hodge, S.G. Yeates, Macromol. Rapid Commun., **2006**, 27, 835; J.M. Lopez Padrosa, M.Bradley, Pigmnet and resin Technology, **2008**, 37(3), 131.
6. M.-B. Madec, D. Crouch, G. R. Llorente, T. J. Whittle, M. Geoghegan and S. G. Yeates, J. Mater. Chem., **2008**, 18, 3230.; D.Y. Shin, P.J. Smith, Journal of Applied Physics, **2008**, 103(11), 114905.
7. M-B.Madec, J. Morrison, M.J. Rabjohns, M.L. Turner, S.G. Yeates, Organic Electronics, **2010**, 11(4), 686-691.;
8. B.J.de Gens, E.Kazanancioglu, J.D.Meyer, U.S.Schubert, Macromol. Rapid. Commun. **2004**, 25, 292.
9. J.J.Cooper-White, J.E.Fagan, V.Tirtaatmadja, D.R.Lester, D.V.Boger, J.Non-Newtonian Fluid Mech. **2002**, 106, 29.
10. B.J. de Gens, L. Xue, U.S. Agarwal, U.S.Schubert, Macromol. Rapid Commun. **2005**, 26, 310.
11. Y.Christianni, L.M.Walker, J.Rheology, **2002**, 46(3), 733.
12. D. Xu, V. Sanchez-Romaguera, S. Barbosa, W. Travis, J. de Wit, P. Swan, S.G. Yeates, J. Mater. Chem., **2007**, 17, 4902.
13. B.J. de Gens, L. Xue, U.S. Agarwal, U.S.Schubert, Macromol. Rapid Commun. **2005**, 26, 310.
14. P.G.de Gennes, J.Chem.Phys. **1974**, 60,5030.
15. A.J.Muller, J.A.Odell, A.Keller, J.Non-Newtonian Fluid Mech. **1988**, 30, 99.
16. J.A.Odell, A.Keller, Y.Rabin, J.Chem. Phys. **1988**, 88(6), 4022.
17. B.A.Buchholz, J.M.Zahn, M.Kenward, G.W. Slater, A.E.Barron, Polymer, **2004**, 24, 1223.
18. J.Frenkel, Acta Physicochim URSS, **1944**, 19, 51.
19. A.F.M. Barton, Handbook of Solubility Parameters and Other Cohesion Parameters, 1985, CRC Press.
20. J.Burke, AIC Book and Paper Group Annual, **1984**, 3, 13-58.
21. W.Macosko, Rheology: Principles, Measurement and Applications, **1994**, VCH, New York.
22. V. Sanchez-Romaguera, Madec, M-B. Madec, S.G. Yeates, Reactive and Functional Polymers, **2008**, 68(6), 1052.
23. S.D. Hoath, I.M. Hutchings, G.D. Martin, T.R. Tuladhar, M.R. Mackley, D. Vadillo, Journal of Imaging Science and Technology, **2009**, 53(4), 041208/1.
24. M.Doi, S.F.Rdwards, "The Theorey of Polymer Dynamics2, **1986**, 1, Oxford University Press.
25. Y.Rabin, J.Polm.Sci. Polym.Lett. Ed. **1985**, 23, 11.
26. Y.Rabin, in Polymer-Flow Interaction, edited by Y.Rabin, **1985**, AIP, New York.
27. A.B. Metzner, A.P. Metzner, Rheol. Acta., **1970**, 9, 174.
28. A.J.Muller, J.A.Odell, S.Carrington, Polymer, **1992**, 33(12), 2598.
29. A.J.Muller, J.A.Odell, A.Keller, Colloid Polym. Sci., **1992**, 270, 307.
30. T.Q. Nguyen, H.H. Kausch, Chimia, **1986**, 40, 129.
31. T.Q. Nguyen, H.H. Kausch, J. Non-Newtonian Fluid Mech., **1988**, 30, 125.
32. T.Q. Nguyen, Q.Z. Liang, H.H. Kausch, Polymer, **1997**, 38, 3783.
33. T.Q. Nguyen, H.H. Kausch, Chimia, **2001**, 55, 147.
34. R.B. Bird, R.C. Armstrong, O. Hassager, Dynamics of Polymeric Liquids, **1987**, Wiley, New York,.

Biogrpahy

Professor Yeates has over 20 years industrial experience working for ICI, Zeneca and Avecia Ltd in the area of specialty polymer chemistry. During that time he held a number of senior technical positions developing and implementing research strategy. Over the last 7 years in industry he developed a particular interest in organic semiconductors and inkjet printing for both industrial and SOHO applications. In November 2004 he was appointed to the full time academic position as Professor of Polymer Chemistry in the School of Chemistry at the University of Manchester.