Molecular weight degradation of synthetic and natural polymers during inkjet print.

Joseph Wheeler1, Khalid A-Alamry1, Stuart W Reynolds2, Steven Lancaster2, Nágila M.P.S. Ricardo3 and Stephen G. Yeates1*
(1) Organic Materials Innovation Centre, School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom
(2) Domino UK Ltd, Bar Hill, Cambridge, CB23 8TU
(3) Department of Organic and Inorganic Chemistry, Polymer Laboratory, Federal University of Ceará CX 12200 Fortaleza, Brazil.

Abstract

We compare the different modes of molecular weight degradation in DOD and CIJ of synthetic vinyl polymers in good solvent and report for the first time extension to polysaccharides This work has significance both in printer design but also in formulation of high molar mass 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 and digital fabrication. There are two major mechanisms through which drops are generated and positioned: continuous inkjet printing (CIJ) and drop-on-demand inkjet printing (DOD). For CIJ and DOD the individual drop generation process and ink management systems present different challenges and constraints on ink design, making them more or less suitable for specific applications. In both technologies the presence of polymer can fulfil a number of functions within the ink formulation ranging from dispersant, viscosity control agent or as the functional material. It has long been recognized that the addition of small amounts of polymeric materials to ink formulations can have a large effect on the printing performance of the ink [1] with both polymer concentration and molecular mass influencing drop ejection and breakup [2].

In this paper we critically compare our recent studies on the degradation of polymer molecular weight in both DOD [3] and CIJ [4] and for the first time report preliminary data on degradation of naturally occurring polysaccharides.

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. Clear solutions in good solvent were prepared by gentle agitation and allowed to stand for 24 hours before use: DOD studies PMMA in γ-butyrolactone and PS in γ-butyrolactone and tetralin; CIJ studies PMMA in methyl ethyl ketone (MEK). For each polymer - solvent combination the overlap concentration c* was defined using the classification of Flory [5] for a flexible polymer in solution, $c^* = 1/[\eta]$ and polymer concentration expressed as a reduced concentration $[\eta].c$ or c/c^*. Galactomannan polysaccharides used in this study were supplied by the Federal University of Ceará, Fortaleza and clear solutions in deionized water were prepared. The overlap concentration c* was defined according to Morris, $4/[\eta]$ [6]. 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

DOD ink-jet printing was carried out using both a MicroJet^{TM} drop-on-demand dispensing device (Microfab, MJ-AB-01, Nozzle diameter (ϕ) = 50 µm, drop velocity (ν) = 2.5 – 5.5 m/s), and a Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix, Inc., Santa Clara, USA, ϕ = 23 µm, ν = 6 - 10 m/s). CIJ printing was performed using a full and deconstructed production model A-Series+ a schematic of which is shown in **Figure 1**. Degradation environments were investigated by passing certain sections of the ink delivery system and printhead to determine the effect of the different regions of this CIJ printer on the polymer solutions. Four distinct print configurations rig were considered:

Rig 1: Full printer: Domino A-Series+ in modulated drop mode (a maximum modulation drive amplitude of 200 V was used). ϕ = 60 µm, ν = 22 m/s. Head temperatures of 27 and 50 °C.

Rig 2: Section B: Ink flow through the full pump system, damper cans and filters circumventing the printhead.

Rig 3: Section A: Ink forced through the printhead by compressed air operating at 3 Bar circumventing the pump system (section B). ϕ = 60 µm, ν = 22 m/s.

Rig 4: Section B: Ink flow through the pump in the absence of filter, damper cans and circumventing the printhead.

Modulation in the context of the CIJ printer is where the ink stream is compressed by a piezo rod at a frequency of 64 kHz in the print head just before it leaves the nozzle. This is to ensure a constant distance between printing drops by increasing the rate of growth of the major varicosity naturally occurring due to the Rayleigh-Plateau instability when a stream of liquid breaks into individual droplets. The maximum drive amplitude was set by applying a 200 V to the drive rod to cause the droplets to detach higher in the printhead; the frequency chosen to obtain the optimum growth rate. For a 75 µm nozzle this is 64 kHz, where for a 60 µm it is 84 kHz. This system is operating just off its optimum performance.

For each fluid, ν was determined stroboscopically, and the strain rate at the nozzle tip (ε) calculated using $\varepsilon = \nu/\phi$.

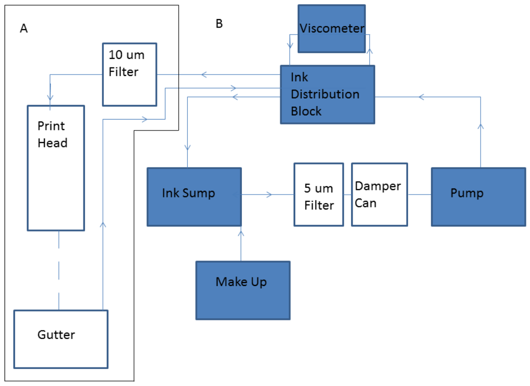

***Figure 1**: Schematic diagram of a full production model A-Series+ (A), and the ink delivery system (B).*

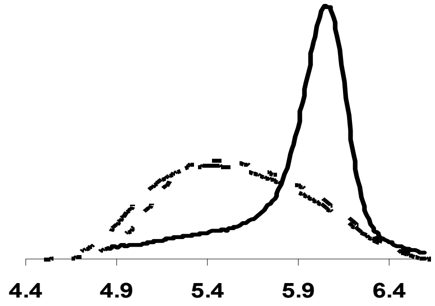

***Figure 3:** Effect of number of sequential passes on the molecular weight distribution (WF/dLogMwt against log mol wt) for PMMA 909K in γ-butyrolactone at c/c* = 0.33 jetted at 50V using a Microfab Printhead at 25 °C. Before jetting (—). Single pass (– – –), double pass (— — —).*

Results and Discussion

Figure 2 shows a composite plot for all PMMA and PS fluids in γ-butyrolactone, and shows the maximum reduced concentration at which jetting was achieved as a function of weight average molecular weight; print head type and drive voltage. The criterion for jetting was taken as visible ligament separation. 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 [3]. We observe that as molecular weight increases it become increasingly more difficult to jet higher concentration fluids [7].

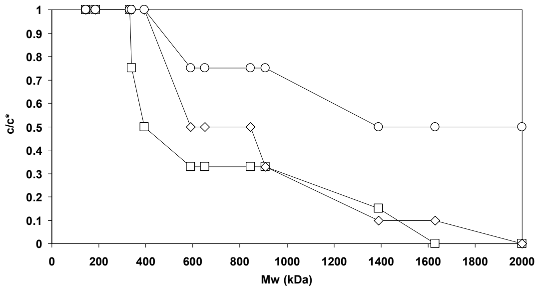

***Figure 2:** Maximum reduced concentration (c/c*) at which inkjet printing was observed as a function of weight average molecular weight for PMMA and PS in γ-butyrolactone at 25 °C using respectively a Microfab Printhead at 30 V (□) and 50V (o) and a Dimatix 10 pl printhead (◊).*

Molecular weight degradation in DOD [3}

The Microfab single nozzle glass capillary represents a low elongational strain rate environment at the nozzle tip between 50,000 – 110,000 s^{-1}. As a consequence polymers having a narrow PDi ≤ 1.3 show no change in molecular weight and distribution, whilst both broad molecular weight distribution 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 more pronounced at low reduced concentration, **Figure 3**. In all cases polymer degradation was essentially complete after a single pass.

On the other hand the Dimatix DMP-2800 represents a much higher elongational strain rate environment at the nozzle tip on drop ejection; 200,000 – 300,000 s^{-1}. Both broad molecular weight and narrow polydispersity PMMA and PS we observed to undergo single pass molecular weight degradation for polymers having M_w between 145 – 590 kDa and 290 – 770 kDa respectively over the concentration range c/c* = 0.15, **Figure 4**, and up to c/c* = 0.5 within these ranges except for PS 770 kDa which only degraded at c/c* = 0.15. The highest molecular weight sample tested PMMA 1390 kDa, PDi = 1.16 did not show molecular weight degradation under any of the conditions tested.

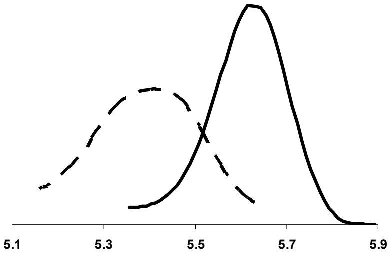

***Figure 4:** (WF/dLogMwt against log mol wt) before (—) and after (– –) single pass jetting for low polydispersity PS 290 kDa in tetralin at c/c* = 0.15 jetted at 18-26 V using Dimatix 10pl DMP Printhead at 25 °C.*

Polymers having weight average molecular weight (M_w) less than 100 kDa show no molecular weight degradation in either printhead configuration which corresponds to a Deborah Number (De) ≤ 1.indicating that the rate of polymer chain relaxation exceeds the rate of polymer chain extension. It is noted that we have calculated the De based upon the residence time within the nozzle. Equally polymers having weight average molecular weight (M_w) greater than around 1,000 kDa show no evidence of molecular weight degradation with De > 25 indicating that the rate of polymer chain extension far exceeds the rate of polymer chain extension giving rise to visco-elastic damping which resists polymer chain degradation.

In the intermediary molecular weight range narrow molecular weight polymers chains break essentially centro symmetrically but only at higher shear rates a consequence of the essentially single Zimm relaxation time of the polymer chain distribution. Broad molecular weight polymers are more prone to molecular weight degradation 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 concentrations, where we approach the concentration where chain interaction in elongational flow (c+) is not possible [8].

Molecular weight degradation in CIJ [4]

The inkjet and degradation behaviour of three linear semi dilute PMMA formulations of differing molecular weight in a CIJ Domino A-Series+ printer has been investigated. This follows on from previous investigations into the degradation of dilute polymeric solutes in DOD printing. The highest molecular weight solution investigated (PMMA 468 kDa) was selected as it is in the centre of the previously reported degradation range for polymer solutes in DOD printing. Furthermore, both cost and sample preparation for ca 1.3 L of monodisperse ultrahigh molecular weight PMMA was not practicable The increase in polymer concentration required for CIJ, c/c* 1.9 – 3.1, in our formulations was found to significantly lower the rate of degradation in CIJ compared to DOD.

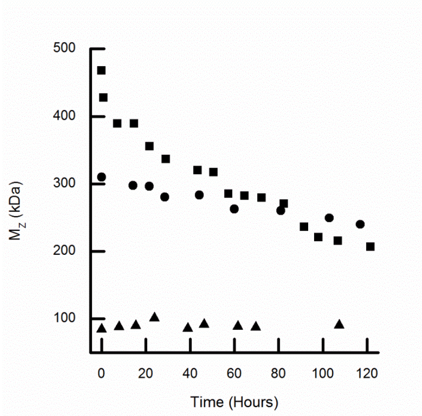

Figure 5: *The development in weight average molecular weight of solutions of PMMA, top to bottom, 468 kDa, PMMA 310 kDa and PMMA 90 kDa after printing in MEK at 50 °C, using a Domino A Series + in modulation mode, Rig 1.*

CIJ shows a similar molecular weight threshold to DOD below which no molecular weight degradation is observed, **Figure 5**. Above this we see a long time constant degradation process where degradation occurs over repetitive average statistical passes through the nozzle. However the most striking result is if we consider the printhead alone, Rig 3, then no significant polymer molecular weight degradation is observed despite the strain rate at the nozzle tip (ε) being of the same order of magnitude to that for a Dimatix DMP-2800 and a Microfab single nozzle glass capillary. In both these systems single pass degradation of high molecular weight polymer was observed [3]. It should also be noted that the flow through the CIJ nozzle is continuous, where it is pulsed in the case of DOD. The calculated maximum strain rates are similar, but one is being periodically switched off and therefore ramped up. This may result in a stronger extensional flow in DOD despite the equivalent strain rates experienced in both systems. This is due to the almost instantaneous acceleration experienced by the polymer solution when it is ejected from the DOD head; whereas in the CIJ system the fluid is in constant motion through the ink system so the acceleration experienced and thus the force experienced by the fluid is lower.

The lack of degradation in the CIJ printhead is believed to be due to a number of factors including the slightly greater nozzle diameter, and different nozzle geometry. The larger nozzle size found in the Domino A Series+ may result in an elongational flow from the printhead rather than a compressional flow; so despite the equivalent shear rate between CIJ and DOD systems no degradation is observed. Alternatively the viscoelastic behaviour of the polymer solution would also become more apparent at higher concentrations. As the concentration increases the number of chain overlaps will increase. When this solution is exposed to an external perturbation such as elongational flow the ability of the solution to respond to this perturbation is not the same as an isolated polymer chain. So whereas a dilute polymer chain would undergo flow induced chain extension and degradation a concentrated solution would dissipate the force by deforming visco-elastically.

The main source of polymer degradation in CIJ printing through a CIJ Domino A-Series+ is found to be passing through the pump alone resulting in mechano-chemical polymer degradation. The random scission degradation is obtained at a lower shear rate through a longer residence time to the mechano-chemical damage in the pump. These results have significance in the total design of inkjet systems for the delivery of high molecular weight polymers and materials sensitive to mechano-chemical degradation and highlight the need for careful consideration when moving from laboratory based print tools to full scale application.

Molecular weight degradation of polysaccharides in DOD

In this work we have considered galactomannan heterogeneous polysaccharides which are used in many different applications including food, pharmaceuticals and paper. They comprise a mainly mannose backbone with galactose side groups (more specifically, a 1,4-linked beta-D-mannopyranose backbone with branch points from their 6-positions linked to alpha-D-galactose, i.e. 1,6-linked alpha-D-galactopyranose) as in **Figure 6**. Specifically we report data for Dimorphandra gardneriana Tul polysaccharide (DM) but similar results have been obtained for other variants.

There are many reports regarding the rheology of galactomannan and due to their complete coil-stretch polymer transition in the dilute to semi-dilute regimes due to the low barrier to free rotation around the ether linkage. Consequently they form viscous solutions or gels even below the overlap concentration in water and consequently we are restricted to printing formulations having c/c* ≤ 0.25.

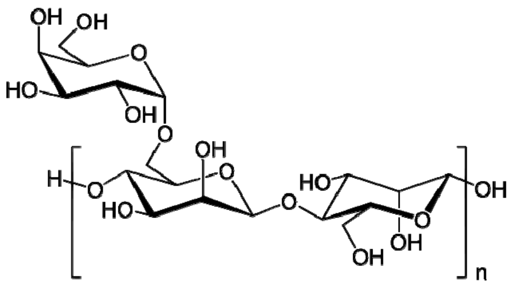

***Figure 6**: A segment of galactomannan showing mannose backbone with a branching galactose unit.*

When ink jetted through a Microfab printhead at very dilute concentrations, c/c* < 0.1, molecular weight degradation is observed. Above this a dramatic single pass decrease in the molecular weight distribution is observed, **Figure 7**. Given the difficulty in getting accurate molecular weight and distributions from GPC in water due to possible aggregation of the polysaccharide the values should be seen as indicative rather than absolute. We calculate the ratio of M_w before printing to M_w after printing to be ca. 30 and M_n before printing to M_n after printing to be > 100.

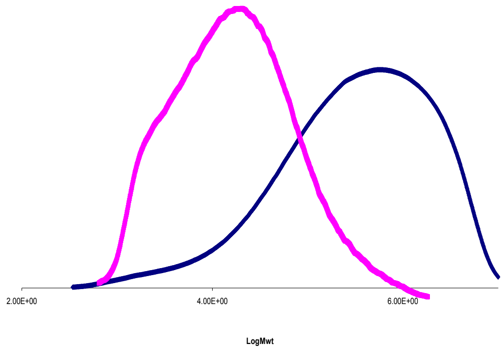

***Figure 7**: (WF/dLogMwt against log mol wt) before (right) and after (left) single pass jetting for DM polysaccharide at c/c* = 0.25 at 50 V using Microfab printhead at 25 °C.*

These observations are not consistent with either centro symmetric bond scission in the case of monodisperse polymer or random scission due to entanglement in the case of polydisperse polymers. It is unlikely that this is a consequence in the difference in bond dissociation energies of C – C main chain in PS and PMMA, $\Delta H^o \approx 332$ kJmol^{-1} against C – O – C in galactomannan polysaccharides $\Delta H^o \approx 341$ kJmol^{-1} which are the same order of magnitude [9]. However a typical O-H …. H hydrogen bond is of the order of 21 kJmol^{-1} and we believe that the significant decrease in molecular weight is a consequence of disaggregation through the breaking of H-bonds with a possible contribution due to main chain C – O – C bond rupture.

Conclusions

We report evidence of flow-induced polymer degradation during inkjet printing for both synthetic and natural polymers as a consequence of the high shear rates experienced during drop generation and ejection. The extent of molecular weight is a inter related function of polymer molecular weight, molecular weight distribution, concentration, polymer architecture, nozzle architecture, holistic printer design and drop generation process. All these factors need to be taken into account when developing stable polymer containing inks

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Biography

Joseph Wheeler is a Ph.D student in the School of Chemistry of the University of Manchester working under the supervision of Professor Stephen Yeates. His research interests are inkjet printing of polymer solutions and fabrication of RFIDs by inkjet printing.