Effect of polymer branching on degradation during inkjet printing

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ABSTRACT

In this paper we demonstrate the potential of high molecular weight hyperbranched methacrylate polymers for inkjet printing. Using the Strathclyde method, a series of hyperbranched poly (methyl-methacrylate) polymers of increasing branch density were prepared. All hyperbranched polymers show both a significantly greater maximum printable concentration compared to equivalent linear polymers with implications for faster print speed. Increasing chain branching above a critical value across the molecular weight distribution was found to result in suppression of molecular weight degradation. This resistance to molecular degradation is because the longest chain segment being much smaller, such that upon jetting the polymer rapidly retains its thermodynamically stable Gaussian coil conformation and the full force of the constrictional flow in the print head is not passed on to the polymer and degradation is supressed. We further go on to show using Electron Paramagnetic Resonance that degradation occurs via a free radical chain scission mechanism.

1. Introduction

Inkjet printing has developed as an important technology for the controlled deposition of functional fluids in applications as diverse as graphics, textiles, biological printing and digital fabrication [1–5]. Two technologies currently dominate the drop generation process, drop on demand (DOD), and continuous inkjet (CIJ). DOD involves the ejection of fluid through a constricted nozzle with a diameter between 10 and 80 μm, through the application of an appropriate pressure wave [6,7]. In comparison CIJ printing consists of a stream of ink passing through a nozzle which breaks up into droplets through the application of a piezo generated continuous acoustic wave. Both approaches have associated formulation challenges and requirements which make them more or less suitable for specific applications [6,7].

The need to deposit soluble functional polymers is important in a number of technology areas including photonics, electronics and biologics [8–12]. High molecular weight and/or high concentration are often desirable for high speed single pass printing and/or to produce a mechanically robust film without the need for post curing technologies. It has long been recognised however that the addition of small amounts of polymer to an ink formulation can have a large and deleterious effect on the print performance with both polymer–solvent interaction, polymer concentration and molecular mass influencing drop ejection and breakup, and leading to formulation compromises [13–15].

At the very high elongational strain rates (γ) experienced in both DOD and CIJ printing, the polymer chain is perturbed from its thermodynamically stable Gaussian coil to a chain extended conformation. If the relaxation time of the polymer from the chain extended state (λ) to its thermodynamically stable Gaussian coil conformation is sufficiently long then the viscoelasticity of the fluid under drop formation and ejection will be strongly influenced [13–15]. The criteria for extended chain persistence is given by the critical Weissenberg number (Wi = $\lambda\gamma_{crit}$) [16–19], and when Wi > 0.5 the majority of a polymer sample will be in the chain extended state. In such studies, λ is typically given by the Zimm relaxation time (λz) since this defines the longest possible chain relaxation of a polydisperse sample [16–19].

It is well documented that above γ_{crit}, there is a further critical strain rate γ_{deg}, which will cause the polymer chain to undergo chain scission; provided it exceeds a critical residence time within

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the high shear environment. As polymer molecular weight increases γ_{crit} and γ_{deg} converge and at a critical molecular weight of *ca.* 5×10^6 Da it is not possible for a polymer to undergo its coil stretch transition without chain scission, with monodisperse polymers being found to break centro-symmetrically and polydisperse samples randomly under elongational flow [16–19].

We have recently reported that the degradation of a linear polymer can occur in both CIJ and DOD if certain criteria are met with regards to molecular weight value, molecular weight distribution, concentration and nozzle geometry [20–22]. Subsequent simulation work supported the assertion that degradation is not due to extensional flow in the ligament after the drop is ejected but rather the high strain rate and constrictional flow in the nozzle itself [23]. However until now we have not considered the role of polymer structure with respect to branching. It is well documented that branching can increase solubility and allow for the formulation of high concentration and low viscosity fluids when compared to those formulations prepared with analogous linear counterparts [24,25]. To date the only consideration of the role of polymer branching in high molecular weight polymers in an inkjet context is by De Gans et al., who showed that the jetting performance and ligament formation properties of 3 and 5 armed star polymers was improved when compared to linear polymers [26].

In this paper we show for the first time hyperbranched polymers, prepared using the experimentally straightforward Strathclyde method [27,28], are capable of being inkjet printed at significantly greater volume fraction than their equivalent analogous linear counterparts with the potentially desirable film forming attributes that high molecular weigh polymers offer, and go on to demonstrate significantly improved resistance to flow induced molecular weight degradation. As a consequence of the greater maximum printable polymer concentration and the higher density of chain ends we are able to provide greater insight into the degradation mechanism using Electron Paramagnetic Resonance (EPR) studies.

2. Experimental

2.1. Materials

All solvents, linear atactic poly(methyl methacrylate) (PMMA; M_w = 90 kDa, Pdi = 2; M_w = 310 kDa, Pdi = 2.8; M_w = 468 kDa, Pdi = 3.3) were obtained from Sigma Aldrich UK and used as received. The solutions prepared with these polymers are referred to as PMMA 90 kDa, PMMA 310 kDa and PMMA 468 kDa throughout this publication. Three hyperbranched PMMA polymers having low, medium and high branching (LB, MB and HB respectively) were synthesised according to the Strathclyde method [27–29] details of which are given in S1. N-tertiary-butyl nitrone (PBN) was obtained from Sigma Aldrich (98%) and used as received. Polymer solutions were prepared by mechanical stirring using a Janke and Kundel RW 20 at 35 °C for 3 h, and filtered using a Buchner funnel with Whatman Qualitative filter paper.

2.2. Instrumentation

Dynamic viscosity measurements were carried out with a Brookfield DVII + viscometer at a temperature of 25 °C (±0.2 °C). All samples were equilibrated in a temperature controlled water bath for 30 min. Intrinsic viscosity measurements were carried out using an Ubbelohde capillary viscometer; dilute solutions ranging from 0.3 to 1.5 g/dl were made up and equilibrated at a temperature of 25 °C (±0.2 °C) for 30 min. The flow time of these solutions through the capillary was measured and the intrinsic viscosity determined by plotting functions of the specific and relative viscosity against

concentration and extrapolating to zero concentration.

Shear stability to ultrasound was carried out using a Missonix 300 ultrasonic probe. All sonication experiments were carried out in an ice water bath to prevent macro heating of the solution. 20 mL of polymer solution was placed in a round bottom flask and the probe submerged in the solution leaving a 5 cm gap between the probe and the bottom of the container. The solution was irradiated at a power between 27 and 33 W.

Drop on demand inkjet printing was carried out using a Dimatix DMP-2800 fitted with a waveform editor and a drop-watch camera system which allows manipulation of the electronic pulses to the piezo jetting device for optimisation of the drop characteristics as it is ejected from the nozzle [20]. CIJ experiments were carried out using a Domino A-Series+ with the printhead removed. This configuration was chosen as previous studies have shown that polymer degradation occurs in both the pump and filters and not the drop formation process itself [22].

Before molecular weight determination, the polymeric materials were precipitated from solution by addition of a large excess of ice cold petroleum ether (40–60 °C bpt) and dried in a vacuum oven. Molecular weights were measured using gel permeation chromatography (GPC) in tetrahydrofuran (THF) comprising a Viscotek GPCmax VE2001 solvent/sample module fitted with 2 × PL gel 10 μm Mixed-B and PLgel 500 Å columns, a Viscotek VE3580 RI and a VE 3240 UV/VIS multichannel detector. The flow rate was 1 mL/min and the system calibrated with low polydispersity PMMA standards in the range of 200 to 2.2×10^6 g/mol, with dodecane as flow marker. Samples were made up to a concentration of 1 mg/ml and pre-filtered using a Whatman 0.45 μm filter. GPC measurements were also performed on a Viscotek TDA305 system using a triple detection capability with a fitted refractometer, viscometer and MALS with methyl ethyl ketone (MEK) as the eluent. Samples were made up to a concentration of 1–5 mg/ml and pre-filtered using Millex 0.45 μm filters. In both GPC systems the columns were heated to 35 °C. A full description of the triple detection GPC methodology and experimental set up is given in S5.

Drop drying experiments were carried out by printing on glass substrates treated with concentrated sulphuric acid and cleaned with distilled water and acetone followed by drying in an oven at 100 °C for 15 min. The analysis of the dried drops was carried out using optical microscopy and atomic force microscopy (AFM).

EPR measurements were carried out using a Bruker EMX Micro X band Spectrometer. Polymer solutions containing PBN spin trap at a concentration of 0.1 M. Solutions were either sonicated or inkjet printing under ambient conditions and subsequently nitrogen purged, frozen in liquid N_2 and thawed prior to measurement.

3. Results and discussion

3.1. Polymer characterisation

The synthesis of the hyperbranched PMMA polymers was achieved using a one-step, 100 g scale solution polymerisation reaction based on the Strathclyde method, S1 [27–29]. The reaction is essentially a linear polymerisation doped with appropriate amounts of a multifunctional monomer, tripropylene glycol diacrylate (TPGDA) and chain transfer agent, dodecanethiol (DDT). The stoichiometric balance between monomer, multifunctional monomer and chain transfer agent is critical in determining whether the polymer maintains solubility throughout the reaction or gels with an insoluble cross-linked network. Ratios of monomer: chain transfer agent: multifunctional monomer and a molecular weight data of the hyperbranched PMMA polymers used in this study are given in Table 1.

Fig. 1a shows the molecular weight distribution of the three