Ink-Jet Printing of Concentrated Polymer Solutions

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Talk

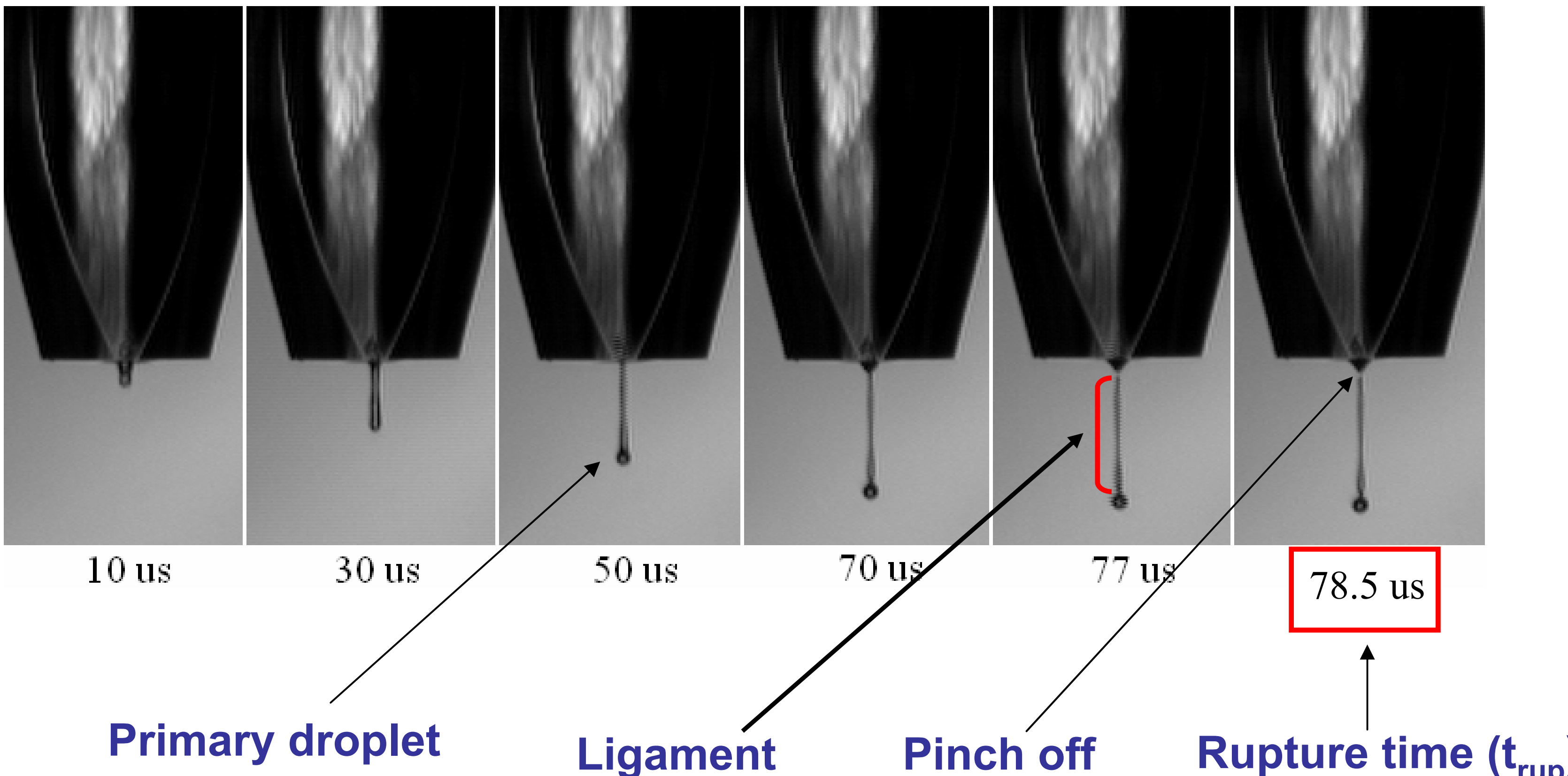
- Motivation
- Experimental
- Effect of molecular weight at overlap concentration
- Effect of polymer concentration through the dilute to semi-dilute and concentrated regime
- Some conclusions

Motivation

- The use of HMW polymer additives is well established in inkjet for use in drag reduction and ligament control at low concentration.
- Demands of graphics, industrial and emerging applications require the deposition of functional polymers at increased concentrations.
- Here we explore the inkjet behaviour of cellulose esters as a model system to look at the effects of molecular weight and concentration for comparatively low molar mass functional polymers.

Inkjet process …

Strobed photo-sequence of a 'typical' polymer fluid



Materials …

Cellulose Ester Polymers

CE	Composition (wt-%)		Hydroxy	M_n (kDa)	PDI
	Acetyl	Butyryl			
1	2	53	1	10.5	2.90
2	2	52	1	30.7	2.49
3	3	50	1	46.5	3.39

Advantages

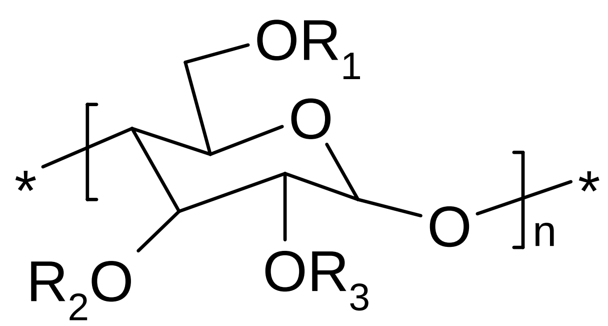
1. Excellent solubility;

2. Comparatively low viscosity;

3. Reduced drying time;

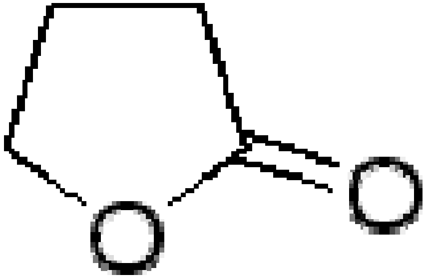
4. Good flow;

5. Good pigment dispersion medium.



Solution Properties: γ-Butyrolactone

CE	[η] (dl/g)	c*	λz (μs)	c (g/dl)	c/c*	η (cP)	γ (mN/m)
1	0.247	4.04	0.53	4.0	1.0	4.2	33.0
2	0.631	1.58	3.43	0.5	0.3	2.2	30.1
				1.0	0.6	2.7	30.6
				1.5	1.0	3.6	31.2
				2.0	1.3	4.7	31.5
				4.0	2.5	11.5	34.0
				6.0	3.8	20.3	35.6
3	1.153	0.86	12.9	0.86	1	4.7	35.0



γ-Butyrolactone

Concentration Regimes

➢Dilute: Polymer chains are at a concentration at which the polymer chains are isolated. Solution concentration rises very slowly with increasing polymer concentration up to the overlap concentration.

➢Semi-dilute: Polymer chains are at a concentration at which they just overlap. This point is called the overlap concentration c*.

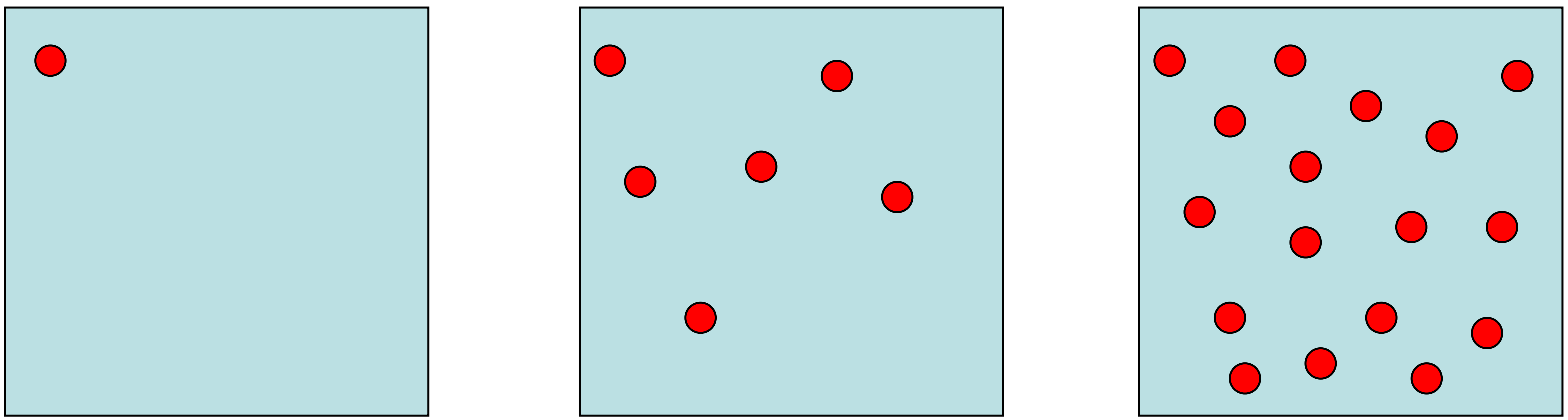
$$C^* = 1/[\eta]$$

➢Concentrated: Polymer chains overlap and viscosity of the solution rises steeply with polymer concentration.

C/C* : reduced concentration

Details …

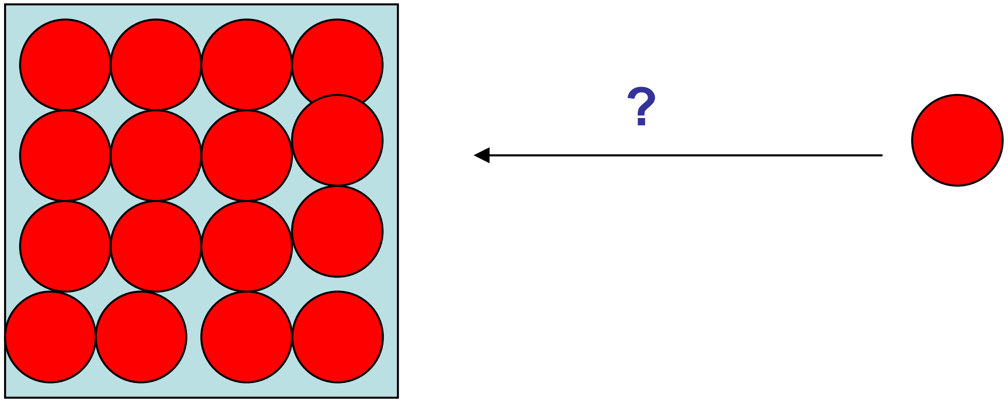
Dilute polymer solution



Increasing polymer Concentration

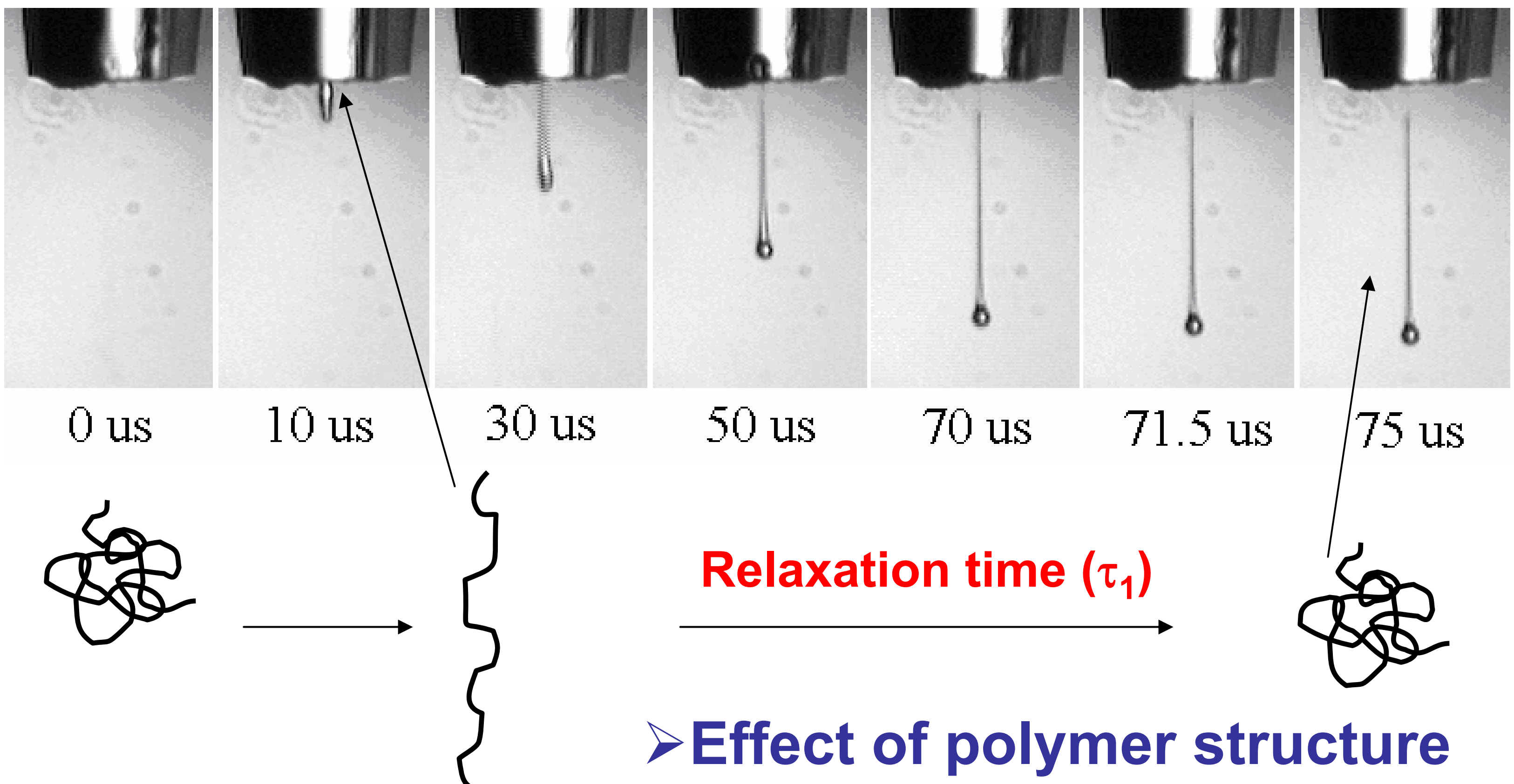
Elasticity of polymer solution increased

Semi-dilute polymer solution



The overlap concentration $c^* = 1/[\eta]$

Complex Fluids Under High Shear



- ➢Effect of polymer structure
- ➢Dilute/semi dilute

Relaxation time (τ_1) …

For dilute polymer solutions the longest relaxation time is given by the Zimm, non free draining relaxation time (τ_1):

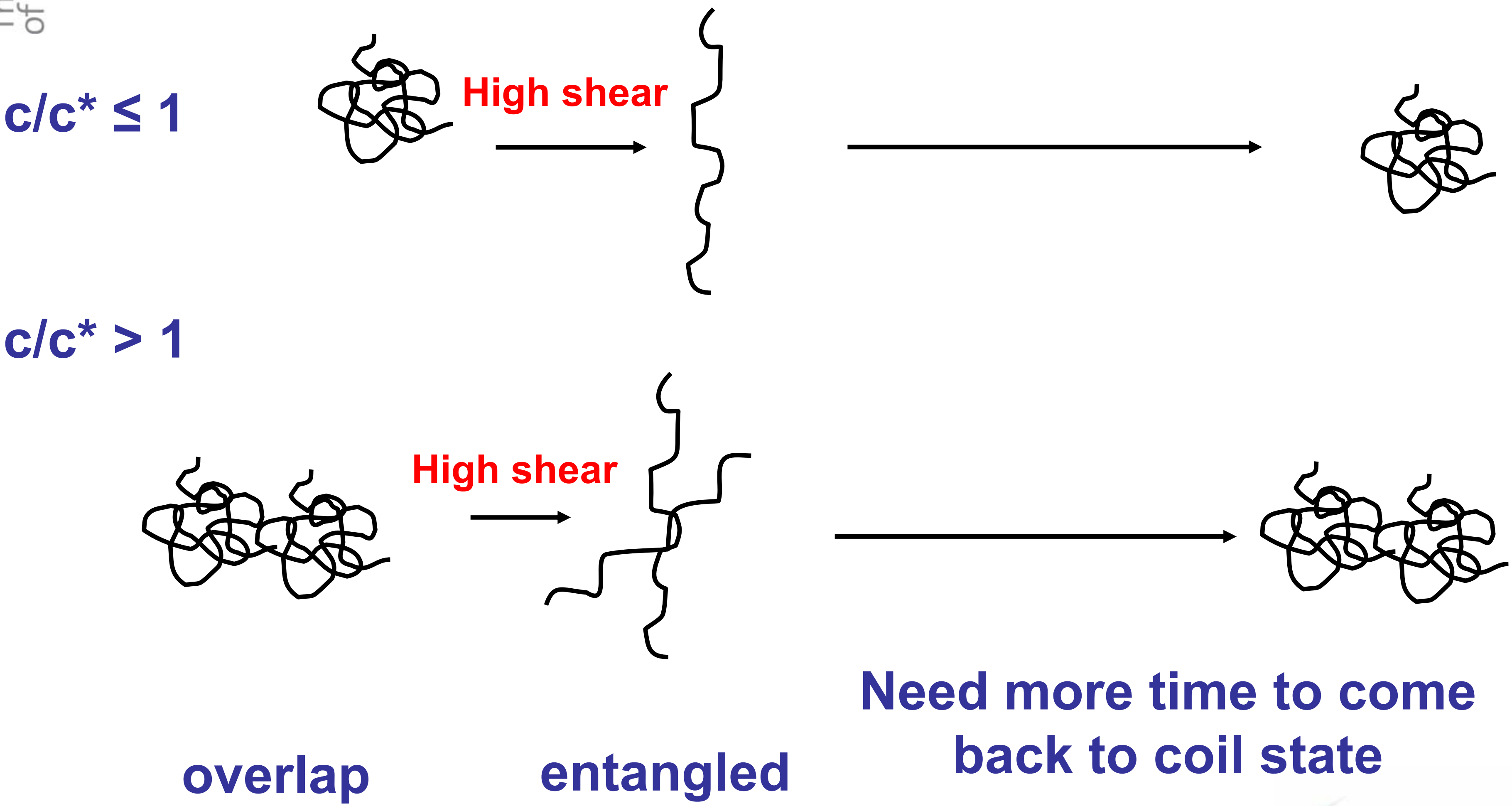
$$\tau_1 = \eta_s[\eta]M/RT$$

where η_s is the viscosity of the solvent, $[\eta]$ the intrinsic viscosity of the polymer solution and M the number average molecular weight.

When the strain is switched off the extended polymer returns to the more thermodynamically stable coil state. It does this slowly because the extended stable chain experiences the full viscous drag of the solvent.

Chain entanglement …

Chain Entanglement During inkjet process



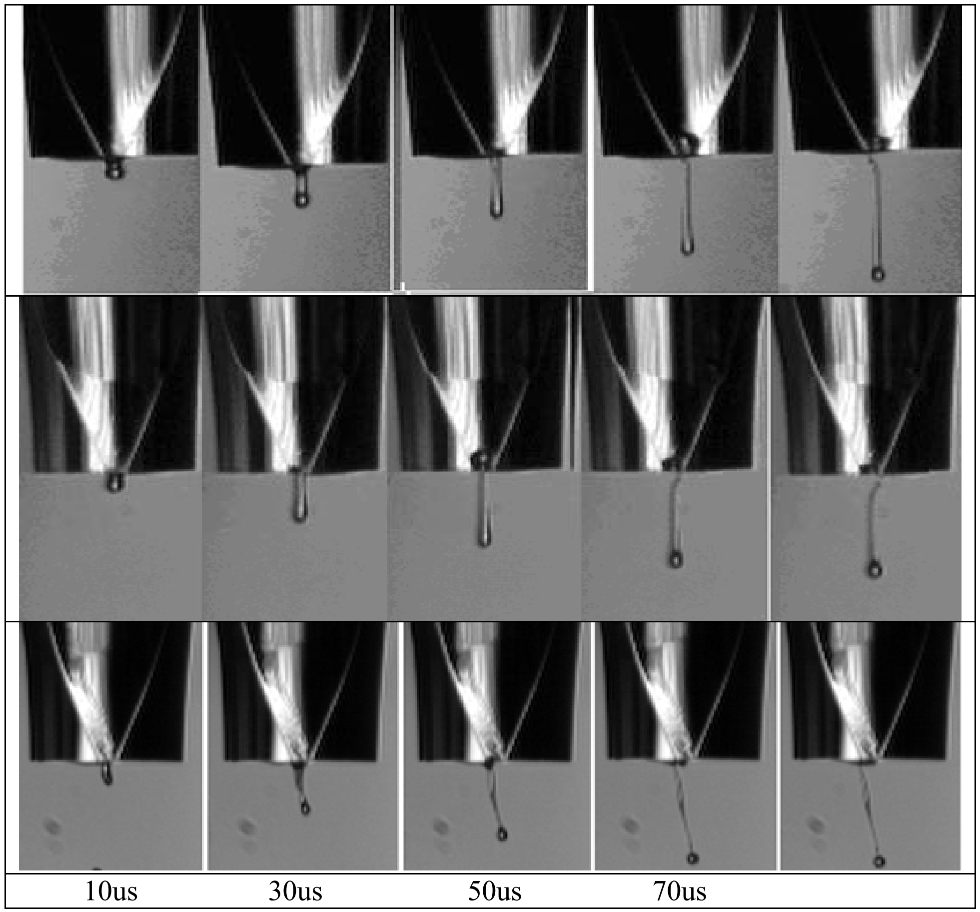
Effect of M_w …

Effect of Molecular Weight at c/c* = 1

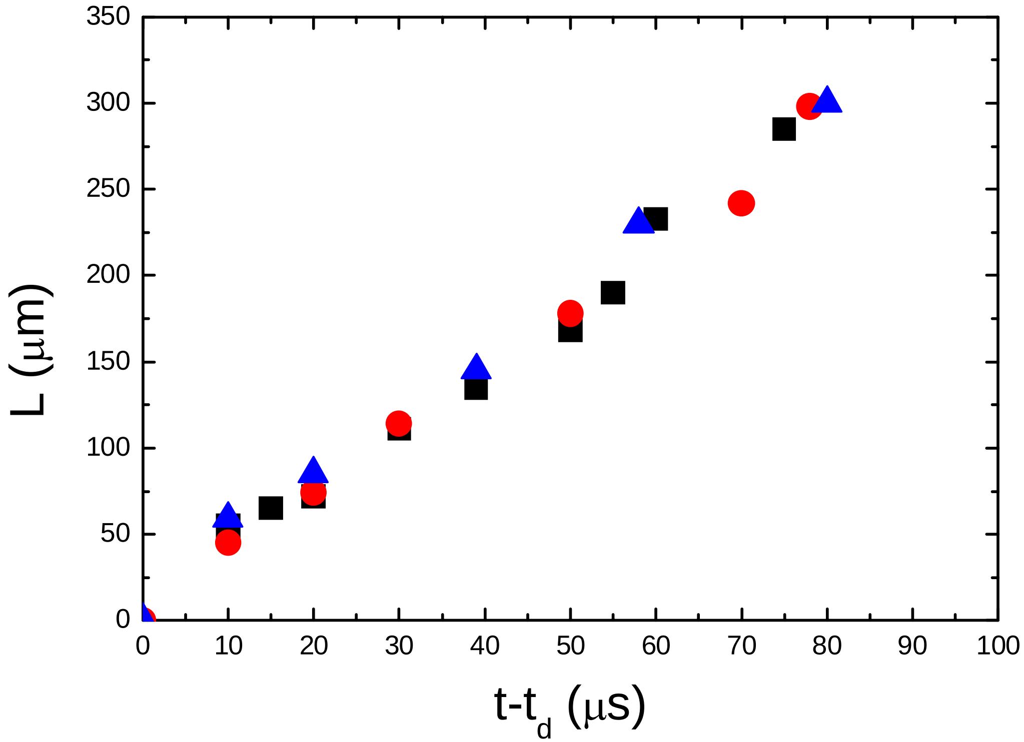
CE1 (4)

CE2 (1.5)

CE3 (0.9)



Effect of Molecular Weight at c/c* = 1



Ligament length at rupture, L_{rup}, as a function of rupture time, t_{rup} = t-t_d.

- **Formulated at c/c* show essentially similar behaviour;**
- **Same ejection velocities for a given waveform.**

Effect of Concentration …

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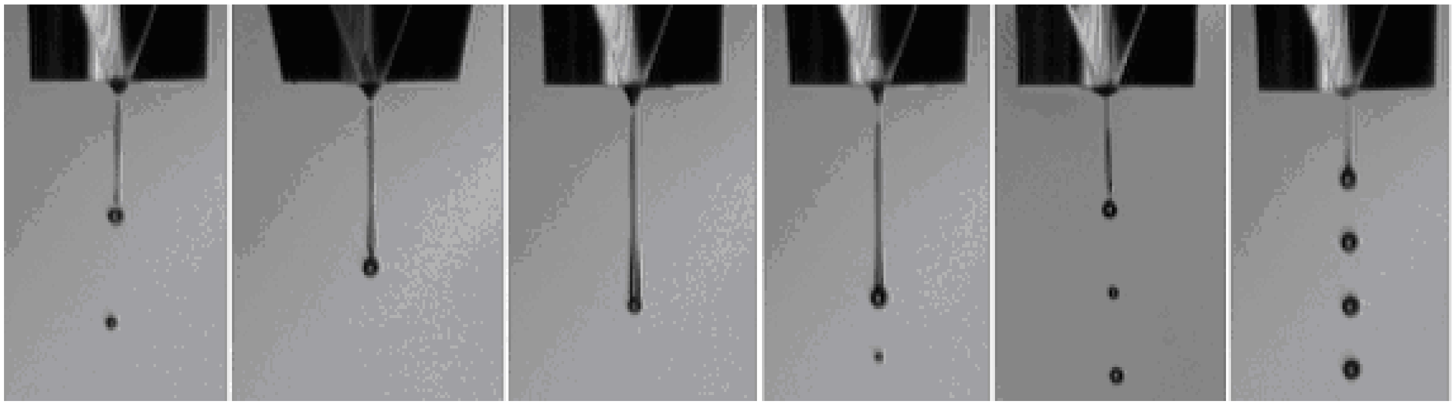
CE2 Effect of Concentration



c/c* 0.32 0.63 0.96 1.28 2.52 3.84

Drop profile at various concentration (applied voltage = 50v).

- **c/c* : reduced concentration;**
- **It is observed that the ligament length at rupture increases up to a reduced concentration of 1 and decreases at higher concentration.**

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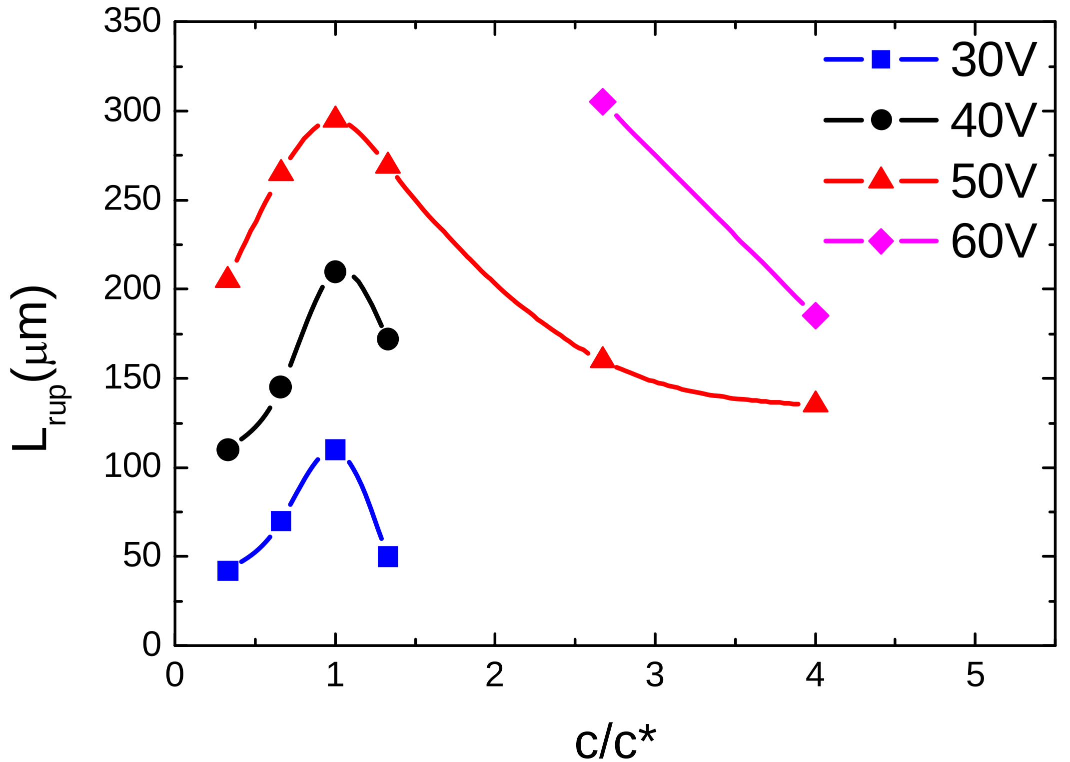
Ligament Length



Ligament length at rupture, L_{rup}, as a function of reduced concentration c/c*.

- **It shows the influence of reduced concentration and applied voltage (30 - 60 V) on the ligament length at rupture (L_{rup});**
- **Maximum L_{rup} is at around the overlap concentration;**
- **L_{rup} decreased rapidly at higher concentrations (c/c* > 1);**
- **Due to chain entanglement.**

L_{rup} Vs. t_{rup} …

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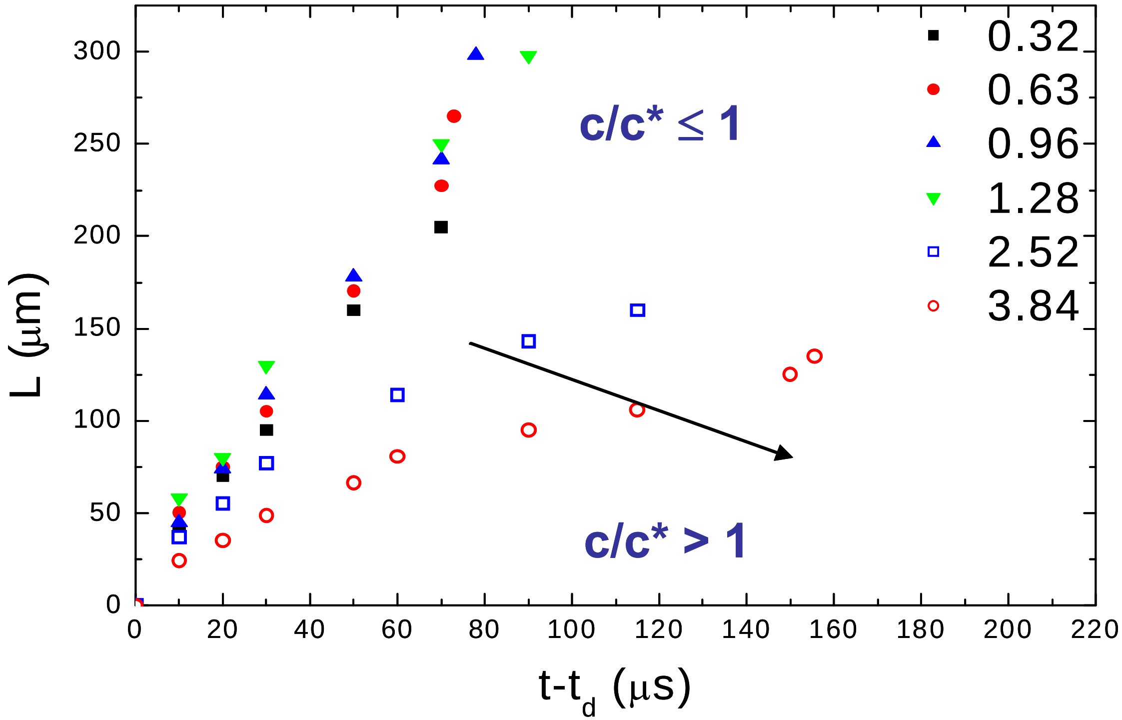
Ligament length as a function of *t - td*



For an applied voltage of 50 V, the travelled distance increases linearly with time and the velocity becomes constant.

- **$t-t_d$ < 20 μs: the trace is independent of polymer C and Mw;**

Interplay of inertia Vs. ST.

- **c/c* ≤ 1: *L-t* data are found to collapse to a single curve;**
- **c/c* > 1: the slope of the curve becomes much shallower and is highly dependant upon concentration.**

Observations …

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Observations

c/c* $\leq$ 1

c/c* > 1

Increasing concentration:

- Rupture time and droplet velocity dominated by applied voltage.

- ligament/droplet velocity decreases significantly;
- Ligaments are shorter and take longer to break;
- If concentration too high no break off.

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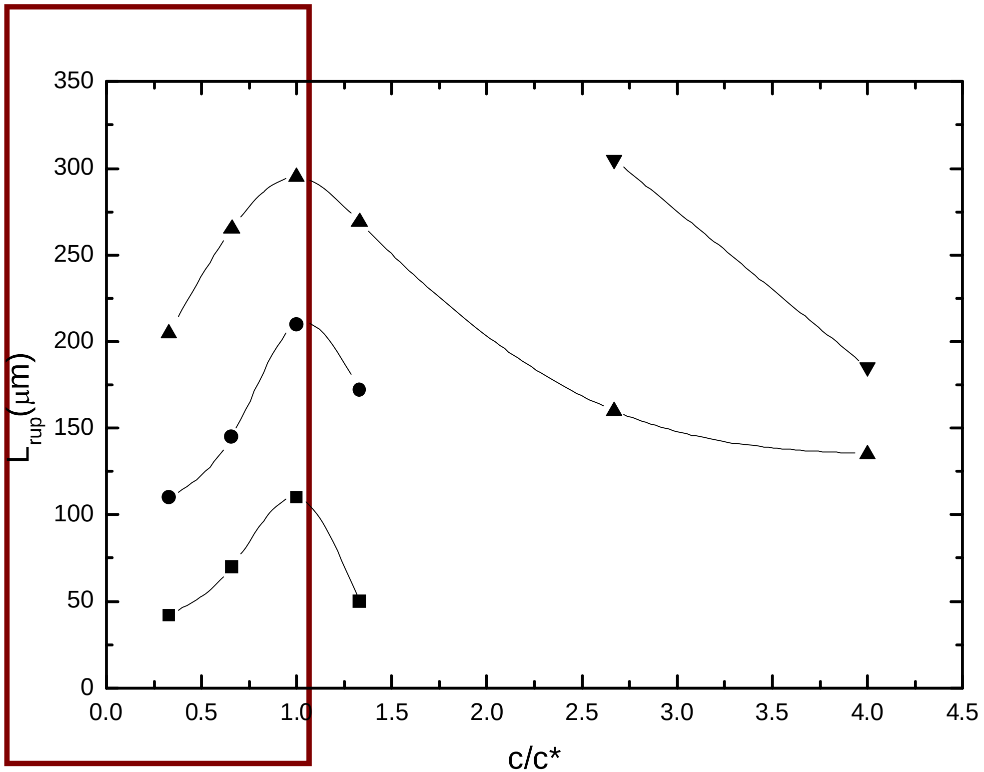

➢**Semi-dilute: Polymer chains started to entangle with each other;**

➢**Concentrated: With the increase of polymer concentration, the entanglement between the polymer chains increased.**

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Conclusions

- **We can now define a series of design rules for the inkjet deposition of polymer containing fluids.**
- **Want τ_1 to be as small as possible so that viscosity increase through hydrodynamic drag is minimized.**

- **Can be achieved by:**

  → **Good solvent for whole polymer chain.**
  → **No aggregation in solution.**
  → **Formulate where possible below C*.**
  → **Lower molecular weight the better.**

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Acknowledgements

- Eastman Chemical Company
- Ministerio de Educacion y Ciencia of Spain
- The Department of Trade and Industry grant TP/2/ED/6/1/10278
- Conductive Ink Technologies