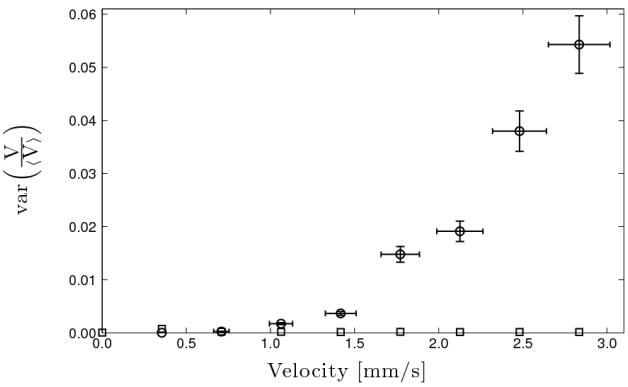

FIG. 7: Fluctuation growth transition. A 120 ppm LMW sample (circles) with a predicted elastic instability at $v_{\rm cr} \approx 2$ mm/s experimentally demonstrates an instability onset at ≈ 1.5 mm/s. Above ≈ 1.5 mm/s fluctuations grow dramatically, as compared to a gentle increase below the observed threshold; polymer free solutions (squares) display no significant fluctuations.

IV. FORMATION OF GLOBULES

We found that at large applied voltages globules would form which appeared to be gelled rafts of polymer (see Fig. 8). The observed structures retained their form while the globule remained in the field of view. These globules only formed in the HMW polymer sample, at higher voltages ($\gtrsim 0.5$ kV) and $c \geq 60$ ppm; at lower voltages, or for the LMW sample at 120 ppm, no indication of gel formation was observed. At the voltages reported in the present study (≤ 0.4 kV) no visual evidence of gel formation was observed in the HMW sample, and at no voltage was gellation observed for the LMW sample.

The mechanism underlying gel formation is likely thermally activated cross-linking at the (Pt) electrode; electrogeneration of polymers at metal surfaces is an established synthesis technique which requires high current densities [43]. The possibility of contact glow electrolysis is discounted as current-voltage characteristics are linear both in the presence and absence of globules, which is not consistent with contact glow electrolysis where linearity is only observed pre-ignition of the plasma [44]. Dip coating [45] the electrodes and intentionally hard drying polymer films in place could either prevent flow, or resulted in globule formation at lower voltages (0.2 kV), and removal of films prevented globule formation at lower voltages. This result supports a high current density/thermal route to globule formation where pin hole or other imperfections in hard dried films would lead to a high local