



Macromolecular relaxation, strain, and extensibility determine elastocapillary thinning and extensional viscosity of polymer solutions

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Delayed capillary break-up of viscoelastic filaments presents scientific and technical challenges relevant for drop formation, dispensing, and adhesion in industrial and biological applications. The flow kinematics are primarily dictated by the viscoelastic stresses contributed by the polymers that are stretched and oriented in a strong extensional flow field resulting from the streamwise gradients created by the capillarity-driven squeeze flow. After an initial inertio-capillary (IC) or viscocapillary (VC) regime, where elastic effects seem to play no role, the interplay of capillarity and viscoelasticity can lead to an elastocapillary (EC) response characterized by exponentially-slow thinning of neck radius (extensional relaxation time is determined from the delay constant). Less frequently, a terminal visco-elastocapillary (TVEC) response with linear decay in radius can be observed and used for measuring terminal, steady extensional viscosity. However, both IC/VC-EC and EC-TVEC transitions are inaccessible in devices that create stretched necks by applying a step strain to a liquid bridge (e.g., capillary breakup extensional rheometer). In this study, we use dripping-onto-substrate rheometry to obtain radius evolution data for unentangled polymer solutions. We deduce that the plots of transient extensional viscosity vs. Hencky strain (scaled by the respective values at the EC-TVEC transition) emulate the functional form of the birefringence-macromolecular strain relationship based on Peterlin's theory. We quantify the duration and strain between the IC/VC-EC and the EC-TVEC transitions using measures we term elastocapillary span and elastocapillary strain increment and find both measures show values directly correlated with the corresponding variation in extensional relaxation time.

polymer physics | rheology | processing | extensional rheology | interfacial flows

Quantitative understanding of the role played by material properties in determining capillary-driven thinning and breakup is critically important for jetting (1–13), dripping (14–20) and dispensing (21–26), liquid-bridge breakup in printing (27–29), atomization and spraying (30–32), drop fission under strong extensional flows (33, 34), and drop and emulsion formation in microfluidics or from membranes (35–39). Longer-lived viscoelastic filaments are also accredited with the stickiness of saliva (40, 41) and deadly fluids produced by carnivorous plants (42, 43), as well as increasing fiber spinnability (44–46). Capillary-driven thinning and pinch-off dynamics of a viscoelastic liquid neck that connects a drop to a nozzle or another fluid element (jet, other drops, or liquid bath) determine the processability of formulations, as well as processing parameters, timescales, and outcomes like drop sizes and size distribution in many industrial and biological applications (2, 3). Streamwise velocity gradients associated with strong extensional kinematics can arise within the thinning liquid necks. Macromolecules can undergo substantial (and sustained) stretching and orientation in shear-free extensional flow fields (47–50), leading to the possibility of coil-stretch transition and hysteresis (48–56), finite extensibility effects (11, 57–63), and, in extreme cases, chain scission (64–66). Consequently,

due to enhanced drag from stretched chains, the polymer solutions display extensional viscosity, η_E (characterizes the resistance to extensional flow) that can be 10 to 10^5 times higher than shear viscosity, η . In contrast, Newtonian solvents exhibit a Trouton ratio, $Tr = \eta_E/\eta$, of three. Understanding and controlling the response of polymer solutions to extensional flows, manifested as delayed thinning and pinch-off, requires characterization and analysis of extensional viscosity, extensional relaxation time, and finite extensibility effects, as well as knowledge of the influence of macromolecular properties on pinch-off dynamics. Such properties cannot be captured by conventional shear rheology characterization or by the use of conventional extensional rheology techniques in which free surface flows are absent, as detailed elsewhere (3–16, 21–26). In this contribution, we carry out a detailed and quantitative analysis of neck-thinning dynamics using dripping-onto-substrate (DoS) rheometry protocols we developed recently (22–26) to probe and report the hitherto unexplored correlations between macromolecular properties (relaxation, strain, and finite extensibility) and the visco-elastocapillary thinning dynamics, advancing our ability to carry out macromolecular engineering of formulations that need to be jetted, printed, sprayed, or dispensed.

Based on the theoretical considerations for local stress balance (incorporating inertial, viscous, capillary, and viscoelastic contributions) (2–4, 57), the radius evolution plots of viscoelastic filaments or necks are expected to show four regimes with distinct kinematics for solutions of flexible polymers: (i) a relatively short initial regime where thinning rate is set by the process that

Significance

Macromolecules are often used as additives to modify flow behavior (rheology and processability) in myriad applications that involve drop formation or liquid transfer. However, processability is usually expressed in heuristic terms like jettability, printability, sprayability, spinnability, and so on and the influence of material properties is poorly understood and characterized. We utilize the recently developed dripping-onto-substrate rheometry to obtain fundamental and hitherto unreported insights into macromolecular properties (strain, relaxation, conformational transitions, and finite extensibility) that influence drop formation dynamics. We anticipate our findings will impact and inspire macromolecular engineering approaches for designing processing-friendly formulations.

Author contributions: J.D. and V.S. designed research, performed research, contributed new reagents/analytic tools, and wrote the paper.

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creates a neck [follows linear stability analysis in jetting (1, 11)], (ii) a Newtonian regime that exhibits self-similar thinning associated with inertio-capillary (67, 68) (IC) or visco-capillary (68, 69) (VC) response [IC or VC, depending upon fluid viscosity (3), detailed later], (iii) an elastocapillary (EC) regime (5, 6, 57–61, 70–74), and (iv) a terminal visco-elastocapillary (TVEC) response due to finite extensibility effects (3, 11, 57–62). Significant progress in understanding of pinch-off dynamics of viscoelastic fluids was enabled by capillary thinning experiments that rely on the creation of a fluid neck by applying step strain to a fluid confined between two plates (3, 58, 59, 70–77), especially using the commercially available technique called CaBER (capillary breakup extensional rheometer). However, pinch-off is completed even before plate separation occurs for low-viscosity ($\eta < 50 \text{ mPa}\cdot\text{s}$), low-elasticity ($\lambda < 1 \text{ ms}$) fluids, including aqueous polymer solutions, and for higher-viscosity/elasticity fluids, the first two stages in neck thinning and the IC/VC–EC transition either get masked or occur during the step-strain stage in the CaBER measurements. The primary extensional rheology measure reported in CaBER and other capillary-thinning-based studies is extensional relaxation time, λ_E , obtained from the decay constant in the exponential fit to the neck radius evolution data in EC regime (5, 6, 11–14, 21–27, 57–62, 70–84). Only a countable few experimental studies (58–62) report the strain and strain-rate-independent value of η_E^∞ or discuss the response in the TVEC regime as the EC–TVEC transition, and presumably the TVEC regime falls below the detection limit of the imaging systems. The inability to investigate the two transitions as well as the response in three out of four regimes using techniques like CaBER that rely on step strain (to create neck) present challenges to a quantitative evaluation of the EC response, the influence of macromolecular properties, and processability.

We have established that the DoS rheometry protocols that rely on the visualization and analysis of the radius evolution of a thinning fluid neck formed between a nozzle and a sessile drop on a substrate allow measurements of extensional relaxation time and pinch-off dynamics of complex fluids (22–26), including low viscosity/elasticity fluids, deemed inaccessible in CaBER measurements. In this paper, using the radius evolution data for semidilute aqueous PEO [poly(ethylene oxide)] solutions of two distinct molecular weights acquired using the DoS rheometry protocols, we report systematic characterization and analysis of both EC and TVEC regimes as well as the two transitions, IC/VC–EC and EC–TVEC, that are typically inaccessible in the CaBER measurements (3, 58, 59, 70–77) and were observed, but not characterized, in the previous DoS rheometry studies (22–26, 80–84). In addition to quantifying the conventional measures including λ_E and η_E^∞ here we introduce and evaluate three additional measures: the scaled EC span, $\Delta t_{EC}/\lambda_E$, the variation in scaled transient extensional viscosity η_E/η_E^∞ [where $\eta_E = \eta_E^\infty(\varepsilon, \dot{\varepsilon}, t)$ is the transient extensional viscosity measured in the EC regime] as a function of Hencky strain, $\varepsilon = 2 \ln(R_0/R(t))$, and the EC strain increment, $\Delta \varepsilon_{EC}$. We report that in semidilute, unentangled solutions of flexible polymers, the three additional measures $\Delta t_{EC}/\lambda_E$, η_E/η_E^∞ , and $\Delta \varepsilon_{EC}$ all show a nearly concentration-independent behavior. We venture to contrast the stress–strain relationship obtained by analyzing the radius evolution data from DoS rheometry with the single chain force extension and the corresponding birefringence–strain relationships. Finally, we elucidate the role of macromolecular relaxation, strain, and finite extensibility in determining the values of η_E^∞ and λ_E as well as the three additional measures, $\Delta t_{EC}/\lambda_E$, η_E/η_E^∞ , and $\Delta \varepsilon_{EC}$ and highlight how our pioneering data acquisition and analysis protocols provide unprecedented access to the physics of stretched polymers and the possibilities for macromolecular engineering of formulations delivered using free surface flows.

Results and Discussion

The DoS rheometry protocols rely on the creation of an unstable, stretched liquid bridge by releasing a finite volume of fluid from a nozzle placed at a fixed distance above a partially wetting substrate and analyzing the shape and radius evolution of the neck that connects a sessile and a pendant drop attached to the nozzle. The DoS rheometry setup is fairly straightforward to build and emulate, as shown schematically in Fig. 1A, and provides versatile measurements of pinch-off dynamics of a whole gamut of complex fluids, as detailed elsewhere (22–24). A comparison of the image sequences with matched time step $\Delta t = 25 \text{ ms}$ for two aqueous solutions of PEO (molecular weight $M_w = 1 \times 10^6 \text{ g/mol}$) with respective concentrations of $c = 0.5$ and $1.5 \text{ wt } \%$ (or c/c^* of ~ 3 and ~ 9) is shown in Fig. 1B and C. Both concentrations lie in the unentangled regime, $c^* < c < c_e$, where the overlap concentration c^* represents the concentration beyond which coil-coil overlap becomes relevant (and solution viscosity, due to polymer contribution, becomes twice the solvent viscosity), whereas the entanglement concentration c_e defines the concentration beyond which topological interactions between chains dramatically reduce their diffusivity, leading to a strong influence on dynamical properties like viscosity. A comparison of the neck shape evolution (see images included in Fig. 1B and C) shows that the delay in pinch-off, quantified as filament lifespan t_f increases with an increase in polymer concentration. The corresponding radius evolution data, obtained by analyzing the neck thinning dynamics for these two solutions, is plotted in Fig. 1D and E, and the IC–EC and EC–TVEC transitions occur at t_c and t_{FE} , respectively. The radius evolution shows that an increase in polymer concentration results in a corresponding increase in EC span, $\Delta t_{EC} = t_{FE} - t_c$, as well as the filament lifespan t_f . Furthermore, Fig. 1D and E show that before the emergence of EC response, the initial neck thinning dynamics are quite distinct, as discussed in more quantitative terms next.

IC, VC, and EC Response. The balance of capillarity and inertia governs the thinning dynamics of low-viscosity fluids like water (2, 10, 16–18, 67) and the initial thinning dynamics of low-concentration polymer solutions (3, 14, 22–26, 74) (including $c = 0.5 \text{ wt } \%$ aqueous PEO solution shown in Fig. 1D). The radius evolution data can be fit by the IC scaling expression given by Eq. 1:

$$\frac{R(t)}{R_0} = X \left(\frac{t_{ic} - t}{t_R} \right)^{\frac{2}{3}}. \quad [1]$$

Here t_{ic} represents the time scale of an inertia-dominated pinch-off process, while t_R represents Rayleigh time $t_R = (\rho R_0^3/\sigma)^{1/2}$ associated with the oscillation frequency of a droplet. Recent computational and experimental studies (19, 20) show that the value of prefactor X is close to 0.4, although the early theoretical and experimental studies (15, 74–76, 85) reported or utilized values in the range of 0.6 to 0.8.

The radius evolution data for a higher-concentration $c = 1.5 \text{ wt } \%$ polymer solution shows a delayed onset of the EC regime. The initial thinning dynamics exhibit a VC response that is governed primarily by a balance of capillarity and viscosity (3, 69) and results in a neck thinning profile that thins linearly over time, as described by the following expression:

$$\frac{R(t)}{R_0} \approx 0.0709 \frac{\sigma}{\eta_0 R_0} (t_p - t). \quad [2]$$

Unlike the Rayleigh time, the VC time, $t_{vc} = \eta_0 R_0/\sigma$, depends upon viscosity. The ratio of two timescales yields a dimensionless measure of viscosity known as the Ohnesorge number,

regime. Carrying out analysis in this shifted time provides more physically reasonable values for G_E . We note that $G_E \neq G \equiv \eta_p \lambda_s$ or the value of G_E cannot be computed using the product of polymer contribution to solution shear viscosity and shear relaxation time. Furthermore, it follows that the radius at IC/VC to EC transition defines the prefactor in Eq. 3 (and radius at this first transition $R_c \approx R_0 (G_E R_0 / 2\sigma)^{1/3}$ is also determined by interplay of elasticity and capillarity). While DoS rheometry allows a robust analysis of both EC regime and λ_E values for semidilute polymer solutions [as detailed in our previous study (22)], Clasen (78) showed that the corresponding analysis of CaBER data is fraught with larger errors, [others showed that comparison with theory often requires the inclusion of a prestretch (57, 73)], and consequently the time span between two transitions and the connections with macromolecular properties and conformational transitions remain unexplored.

Radius Evolution in the TVEC Regime. In the EC regime, filament thinning proceeds with a constant extensional rate such that the effective Weissenberg number, $Wi_E = \dot{\epsilon} \lambda_E = 2/3$ is the same for all measurements despite molecular weight or concentration variations, even though the thinning rate and the actual extensional rate for each fluid is set by its extensional relaxation time. Although the strain rate exhibits a constant value, the Hencky strain $\epsilon = 2 \ln(R_0/R(t))$ increases monotonically, accompanied by a progressive buildup of macromolecular strain and orientation, which leads to the emergence of the TVEC regime due to the finite extensibility effects. Although the extensional rate remains constant in the EC regime, after the EC–TVEC transition occurs at the instant t_{FE} , the extensional rate rises again. In the TVEC regime, the extensional viscosity value reaches its terminal, steady-state value, and the radius evolution can be described by the following expression (3, 90):

$$\frac{R(t)}{R_0} = \frac{\sigma}{2R_0\eta_E} (t_f - t) = \frac{1/2}{Oh Tr^\infty} \left(\frac{t_f - t}{t_R} \right). \quad [4]$$

Here $Tr^\infty = \eta_E^\infty / \eta_0$ is the terminal Trouton ratio and $Oh = \eta_0 / \sqrt{\rho\sigma R_0}$. The value of Rayleigh time t_R is ~ 2 ms for PEO solutions (computed using outer nozzle radius), and t_f refers to the filament lifespan. The existence of steady, terminal extensional viscosity implies that there is an upper bound to the viscoelastic stresses that can be generated from the interplay between the effect of stretching and orientation.

Viscoelastic Fluid Necks Persist for Longer Duration than Captured in Radius Evolution Data. The minimum size of a fluid neck that can be resolved is determined by the resolution of the imaging system. However, due to constraints on working distance, depth of field, and the resolution possible with visible light, feature sizes below 1 μm are hard to track and, practically, most visualization methods stay above a minimum radius of 5 μm . However, even if the image analysis appears to return a constant thickness that corresponds to the minimum size recorded per pixel, the real fluid neck can persist and continue thinning, as is demonstrated in Fig. 1 *F* and *G*. The two space–time diagrams are constructed by stacking together cropped images that are one pixel wide and belong to the region highlighted in blue in Fig. 1 *B* and *C*. The image stack is rotated by 90° to show time on the x axis (linear) such that a time step of $\Delta t = 1/\text{fps}$ exists per pixel. The duration for which a neck persists can be visualized in terms of the total number of frames included in these backlit images. The TVEC regime as observed in Fig. 1 *D*, *E*, *F*, and *G* is usually approached once the radius of a filament becomes quite small (typically below a dimensionless radius $R(t)/R_0 \leq 10^{-2}$). The initial radius in both space–time diagrams shown in Fig. 1 *F* and *G* is taken to be equal to the nozzle radius ($R/R_0 = 1$). The space–time dia-

gram for the two PEO solutions captures the difference in IC and VC dynamics in the initial region, and shows that the IC–EC transition for lower concentration PEO solution, visible in Fig. 1 *F*, is more abrupt than the VC–EC transition manifested in Fig. 1 *G*. The space–time diagram shows that the fluid necks persist far beyond the instant for which the last data point is recorded in the radius evolution data and beyond the value of t_f determined from the TVEC fit.

Radius Evolution and Extensional Viscosity of Aqueous Semidilute PEO Solutions. Fig. 2*A* shows the radius evolution plot for dilute and semidilute aqueous PEO solutions of two molecular weights ($M_w = 1 \times 10^6$ and 2×10^6 g/mol, respectively). As all solutions (except $c = 2$ wt %) display an initial IC response, their behavior appears indistinguishable before t_c , or before the viscoelastic effects are manifested. After t_c , the EC regime sets in and the radius evolution shows a concentration-dependent decrease in slope (as the extensional rate is inversely proportional to the extensional relaxation time) and an increase in pinch-off time with an increase in polymer concentration. The concentration-dependent delay in the pinch-off event implies that the more elastic solutions display a higher resistance to capillary-driven flows that drive the neck-thinning dynamics.

The ratio of capillary stress to extensional rate can be used for estimating this resistance to extensional flow, leading to the following formula for determining transient as well as steady, terminal extensional viscosity values from the radius evolution data:

$$\eta_E = \frac{\sigma}{R(t)\dot{\epsilon}} = -\frac{\sigma}{2dR(t)/dt}. \quad [5]$$

The extensional viscosity data, computed using Eq. 5, are shown as a function of accumulated Hencky strain in Fig. 2*B* for a range of PEO concentrations. Since the extensional rate remains constant during the EC regime, the transient extensional viscosity, $\eta_E = \eta_E^t(\epsilon, \dot{\epsilon}, t)$, values are plotted as a function of Hencky strain that increases monotonically in both EC and TVEC regimes. However, beyond the EC–TVEC transition (or in the finite extensibility regime), the computed extensional viscosity values appear to reach a terminal steady-state value (η_E^∞), as can be observed in Fig. 2*B*. The magnitude of both transient and terminal extensional viscosity increases with an increase in polymer concentration or molecular weight, and trends shown in Fig. 2 are consistent with data included in our previous study (22). Quite remarkably, the datasets acquired for semidilute solutions appear to have similar strain-dependent increase, and hence in Fig. 3*A* we present the data for the semidilute solutions in terms of viscoelastic stress vs. strain comparison. Due to the remarkable similarity in shape of all curves, we decided to pursue a deeper understanding of the underlying macromolecular dynamics, strain and relaxation, as discussed next.

Macromolecular Strain, Fluid Strain, Birefringence, and Force–Extension Curve. Historically, extensional rheology characterization using four-roll mills (91–94), opposed-jet rheometer (64, 95, 96), or stagnation-point flows in microfluidic devices (41, 97) has relied on the measurement of flow-induced birefringence, Δn , in response to different extensional rates. The birefringence of polymer solutions tracks the macromolecular conformational changes, for both change in coil dimensions and the difference in polarizability along the length of a segment and perpendicular to it contribute to the difference in polarizability at the chain level (91, 92, 98). The well-documented correspondence between the extensional stress and flow-induced birefringence can be expressed by using the stress-optical rule with $\eta_E \dot{\epsilon} = \Delta n / C$, where C represents the stress-optical coefficient (with a caveat that the stress optical rule is expected to break down for large strains). As the extensional rate $\dot{\epsilon} = 2/3\lambda_E$ in the EC regime is a constant, we

additional measures, $\Delta t_{EC}/\lambda_E$, η_E/η_E^∞ , and $\Delta \varepsilon_{EC}$. In semidilute, unentangled aqueous solutions of PEO, we find that the scaled EC span, $\Delta t_{EC}/\lambda_E$, and the increase in extensional stress ($\tau_E = \eta_E \dot{\varepsilon}$) with Hencky strain show a nearly concentration-independent behavior. For the semidilute aqueous PEO solutions the EC span is measured to be around $6\lambda_E$ and we show that the EC span and the terminal extensional viscosity value are all directly proportional to extensional relaxation time. As EC span contributes to the delay in pinch-off on addition of polymers, we establish a connection between the EC span and the values of surface tension, terminal extensional viscosity, extensional relaxation time and the effective extensional modulus. Furthermore, we determine that a connection can be made between the transient extensional viscosity vs. Hencky strain as evaluated from the capillary-thinning-based DoS measurements and the flow-induced birefringence–macromolecular strain relationship. Even though the capillary-driven thinning dynamics for flexible polymers including PEO solutions have been investigated before using DoS rheometry as well other techniques (including CaBER, jetting, and dripping), the connection between the extensional stress, fluid and apparent macromolecular strain, and extensional relaxation time shown in this study have not been discussed or reported before. We anticipate the experimental and theoretical arguments presented herein will provide inspiration for additional experiments for polymers with different chemical structures as well as for a better understanding of stretched-chain hydrodynamics.

Materials and Methods

Aqueous solutions of PEO (Sigma-Aldrich) of two molecular weights (average molecular weights are 1,000 and 2,000 kg/mol) were prepared in deionized water. The computed critical overlap concentration values are respectively 0.17 wt % and 0.1 wt %, and the estimated values of Zimm relaxation times are 0.1 ms and 0.35 ms. The concentration of solutions reported in this study range from $c/c^* = 0.1$ to $c/c^* = 10$. Separately, extensive characterizations for both dilute and semidilute (22) solutions were previously carried out. The critical overlap concentrations, c^* , were calculated using the formula

$c^*[\eta] \approx 1$ and the Mark–Houwink–Sakurada equation, $[\eta] = KM_w^a$. Intrinsic viscosity $[\eta]$ depends on the molecular weight of the polymer, and the values of the coefficient $K = 1.25 \times 10^{-2}$ mL/g and the exponent $a = 0.78$ are listed in the polymer handbook data (106).

The DoS rheometry setup shown in Fig. 1A includes a dispensing system, nozzle, substrate, and imaging and image analysis system. Discrete fluid volumes for the DoS extensional rheometry experiments are deposited onto a glass substrate placed a distance H below the nozzle using a New-Era syringe pump. A stainless-steel nozzle with an inner diameter of $D_i = 0.838$ mm and an outer diameter of $D_o = 1.270$ mm is used. The fluid is delivered at a relatively low flow rate, Q , and pumping is stopped after the drop touches the substrate. The fluid that is pumped out of the nozzle eventually spreads on a solid substrate, and the unstable liquid bridge formed undergoes capillary-driven self-thinning and breakup. The aspect ratio, H/D_o , was selected to be around 3. Quantitative analysis of progressive filament thinning requires the measurement of neck radius as a function of time. Unlike CaBER that relies on a laser-based diameter measurement, in the present setup the thinning neck radius is determined from videos captured using a high-speed imaging system, and the neck shape is always visualized and recorded. The high-speed imaging system consists of a Photron Fastcam SA3 high-speed camera equipped with a Nikkor 3.1× zoom lens (18 to 50 mm) and a supermacro lens. We place a limit to a minimum value of a liquid diameter that can be resolved to 10 μm . This value is slightly above the resolution limit imposed by the imaging system used in this study. The capillary-driven thinning dynamics are captured at a rate of 8,000 to 25,000 frames per s (fps). The movies are analyzed using specially written codes using ImageJ and MATLAB. Each measurement is repeated at least five times, and a good reproducibility is observed. Further details about the DoS rheometry setup, contrast with other techniques that use capillary-driven thinning and breakup measurements, and measurement of concentration-dependent extensional relaxation time of neutral and charged polymer solutions can be found in our previous publications (22–26).

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