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

Jelena Dinic^a and Vivek Sharma^{a,1}

^aDepartment of Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607

Edited by Alexis T. Bell, University of California, Berkeley, CA, and approved March 21, 2019 (received for review November 28, 2018)

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 inertiocapillary (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

uantitative understanding of the role played by material Q 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). Capillarydriven 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-ontosubstrate 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.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10. 1073/pnas.1820277116/-/DCSupplemental.

Published online April 12, 2019.



Published under the PNAS license.

¹To whom correspondence should be addressed. Email: viveks@uic.edu.

creates a neck [follows linear stability analysis in jetting (1, 11)], (ii) a Newtonian regime that exhibits self-similar thinning associated with inertiocapillary (67, 68) (IC) or viscocapillary (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_F^{∞} 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 $\eta_E = \eta_E^t(\varepsilon, \dot{\varepsilon}, t)$ 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 $\Delta t = 25$ ms for two aqueous solutions of PEO (molecular weight $M_w = 1 \times 10^6$ g/mol) with respective concentrations of c = 0.5 and 1.5 wt % (or c/c^* of \sim 3 and \sim 9) is shown in Fig. 1 *B* 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. 1 B 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. 1 D 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. 1 D 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 wt % aqueous PEO solution shown in Fig. 1D). The radius evolution data can be fit by the IC scaling expression given by Eq. 1:

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

Here t_{ic} represents the time scale of an inertia-dominated pinchoff 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 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:

$$\frac{R(t)}{R_0} \approx 0.0709 \frac{\sigma}{\eta_0 R_0} \left(t_p - t \right).$$
^[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,



Fig. 1. DoS rheometry setup and representative radius evolution plots and space-time diagrams. (*A*) DoS rheometry setup consists of an imaging system that includes a high-speed camera with additional lenses and a dispensing system that includes a syringe pump connected to a nozzle. (*B*) The sequence of images for the aqueous PEO solution ($M_w = 1 \times 10^6$ g/mol and c = 0.5wt %) obtained at 8,000 fps shows the formation of slender, cylindrical neck that emerges due to EC thinning response. (*C*) The sequence of images for the PEO solution ($M_w = 1 \times 10^6$ g/mol and c = 0.5wt %) obtained at 8,000 fps shows the formation of slender, cylindrical neck that emerges due to EC thinning response. (*C*) The sequence of images for the PEO solutions ($M_w = 1 \times 10^6$ g/mol and c = 1.5wt %) shows a delayed breakup in contrast with *B*. (*D* and *E*) Radius evolution over time plotted for the PEO solutions with c = 0.5wt % and c = 1.5wt %, obtained by analyzing neck shape and neck radius evolution over time. The neck radius is scaled using nozzle radius, $2R_0 = 1.27$ mm. (*F* and *G*) Space-time diagrams for the two PEO solutions highlight the difference in the initial dynamics and transitions, as well as show that the neck persists beyond the minimum resolvable radius, and filament lifetime is longer than the lifespan apparent from the radius evolution plots.

 $Oh = t_{vc}/t_R = \eta_0/\sqrt{\rho\sigma R_0}$, after von Ohnesorge (86), an early pioneer in the field of drop formation. The ratio depends upon the relative importance of viscous and inertial effects and the VC response is observed for Oh > 1 values. Here, t_p is the IC pinchoff time. For both molecular weights, as Oh < 0.1 for $c/c^* < 4$, the IC regime, followed by EC and TVEC regimes, can be observed and analyzed, even though similar measurements are well below the range of CaBER-based measurements [see the detailed analysis of the measurable range with CaBER measurements by Rodd et al. (74)].

The radius evolution data for both solutions (Fig. 1 *D* and *E*) show a clear transition to the EC regime after time t_c . The transition is delayed for higher-concentration PEO solutions with higher viscosity and elasticity. The transition to the EC regime is accompanied by a significant decrease in thinning rate $\dot{R} = -dR/dt$ as well as the extensional rate defined as $\dot{\varepsilon} = -2\dot{R}(t)/R(t)$. The radius evolution data in the EC regime appears as a straight line on the semilog plots, implying the

data can be fit by a decaying exponential function of the following form:

$$\frac{R(t)}{R_0} \approx \left(\frac{G_E R_0}{2\sigma}\right)^{1/3} \exp[-(t-t_c)/3\lambda_E].$$
 [3]

Even though expression **3** is based on the theoretical and experimental results by Entov, Yarin, and coworkers (4–6, 57–59, 70– 72), Renardy (87), and McKinley, Clasen, and coworkers (3, 10– 14, 21, 27, 43–45, 60, 61, 73–76, 79, 88), among others (22–24, 49, 50, 77, 80, 81), the specific form of Eq. **3** and the parameters included differ from the most often cited Entov–Hinch expression (57) and the expression suggested by Zhou and Doi (89). Here G_E and λ_E are defined as the extensional elastic modulus and the longest extensional relaxation time, respectively, implying these are distinct from the corresponding values that can be obtained from shear rheology characterization. The form given in Eq. **3** includes a timescale t_c defined at the onset of the EC 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 $\varepsilon = 2 \ln(R_0/R(t))$ 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):

$$\frac{R(t)}{R_0} = \frac{\sigma}{2R_0\eta_E} \left(t_f - t \right) = \frac{1/2}{Oh} \frac{t_f - t}{Tr^{\infty}} \left(\frac{t_f - t}{t_R} \right).$$
[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 $R(t)/R_0 \le 10^{-2}$). 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 diagram 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. 24 shows the radius evolution plot for dilute and semidilute aqueous PEO solutions of two molecular weights $(M_w = 1 \times 10^6 \text{ and } 2 \times 10^6 \text{ g/mol}$, 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 concentrationdependent 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:

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

The extensional viscosity data, computed using Eq. 5, are shown as a function of accumulated Hencky strain in Fig. 2B for a range of PEO concentrations. Since the extensional rate remains constant during the EC regime, the transient extensional viscosity, $\eta_E = \eta_E^t(\varepsilon, \dot{\varepsilon}, t)$, 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. 2B. 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. 3A 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 $\eta_F \dot{\varepsilon} = \Delta n/C$, 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 $\dot{\varepsilon} = 2/3\lambda_E$ in the EC regime is a constant, we



Fig. 2. Decrease in neck radius and variation in extensional viscosity measured for the aqueous PEO solutions in the dilute and semidilute regime. (A) Radius evolution plot for PEO solutions of two molecular weights ($M_w = 1 \times 10^6$ g/mol and $M_w = 2 \times 10^6$ g/mol, with respective overlap concentration, c^* , of 0.17 wt % and 0.1 wt %). The time axis is shifted using IC/VC–EC transition point, t_c . The initial IC response shows no dependence on viscosity or elasticity (for all solutions with $c/c^* < 4$ with relatively small Ohnesorge number, Oh < 0.1 exhibit IC regime). However, both extensional relaxation time and the EC span get longer with increase in polymer concentration or molecular weight. (*B*) Extensional viscosity as a function of Hencky strain accumulated after IC/VC–EC transition; the measurements shown rely on the radius evolution data shown for the PEO solutions in *A*.

choose to plot extensional stress as $\eta_E \dot{e}$ as a function of change in accumulated Hencky strain in Fig. 3*A*. Before proceeding to utilize the postulated correspondence, we first need to summarize the relationships between flow birefringence and macromolecular strain.

Let us assume that the flexible macromolecule can be modeled as an equivalent chain comprised of N_K Kuhn segments, each of a Kuhn length b_K and the unperturbed, unstretched coil size R_{us} is stretched to a size R_s , such that for fully unraveled chain the maximum value of R_s equals the contour length $R_s = R_{max} = N_K b_K$. Let us assume that the R_{us} and R_s values correspond to the rootmean-square size, ensemble-averaged, with solvent-quality and flexibility effects included. Combining ideas from the work of Treloar (99), Kuhn and Grün (100), and Peterlin (101, 102) (and the related discussions in refs. 98 and 103) and by defining the fractional chain extension as $\beta = R_s/R_{max}$, the birefringence of stretched chains (scaled by birefringence at full chain extension, Δn_0) can be written using the inverse Langevin function, $L^{-1}(\beta)$, as an empirical series expansion:

$$\frac{\Delta n}{\Delta n_0} = 1 - \frac{3\beta}{L^{-1}(\beta)} \cong \frac{3}{5} \beta^2 + \frac{1}{5} \beta^4 + \frac{1}{5} \beta^6.$$
 [6]

For intermediate strains, the normalized birefringence $\Delta n / \Delta n_0$ can be considered to be representative of the scaled extensional stress difference. As the extensional rate in the EC regime and at the EC-TVEC transition is the same, the scaled extensional stress can be written as $\eta_E^t/\eta_E^\infty = \eta_E/\eta_E^\infty$ and we effectively plot the scaled stress, η_E/η_E^{∞} , against the normalized fluid strain, $\varepsilon/\varepsilon_{FE}$, extracted from DoS measurements in Fig. 3B. Both η_E^{∞} and ε_{FE} are calculated using radius evolution data in the TVEC regime (and are presented in Table 1). The scaled birefringence versus scaled fractional strain curve Eq. 6 shown in black stars in Fig. 3B appears to qualitatively agree with the normalized extensional stress (viscosity) vs. strain curve. However, for a majority of datasets, expression 6 overpredicts birefringence or degree of chain stretching values for small extensions compared with the experimentally determined fluid strain curves and underpredicts the degree of stretching obtained in experiments for larger strains. Despite these differences, the correspondence between the experimentally determined exten-

8770 | www.pnas.org/cgi/doi/10.1073/pnas.1820277116

sional stress-Hencky strain curves obtained from DoS rheometry and the theoretical birefringence-molecular strain curves is both remarkable and insightful.

Fig. 3C plots the EC strain increment, $\Delta \varepsilon_{EC} = \varepsilon_{FE} - \varepsilon_c$, defined as the difference in the value of Hencky strain values determined at the two transitions points for an extended range of data. We find that $\Delta \varepsilon_{EC}$ displays a value that is nearly independent of concentration or molecular weight, and equivalently the ratio of the filament radius at the two transitions is concentration/ molecular-weight-independent. In contrast, the terminal extensional viscosity values shown in Fig. 3D display a strong dependence on both concentration and molecular weight. The values of terminal extensional viscosity increase with concentration, and for matched polymer concentration, the highermolecular-weight solution exhibits higher terminal extensional viscosity. The η_F^{∞} data for additional molecular weights is included in SI Appendix, Supplementary Information, and a detailed investigation of λ_E for semidilute solutions is published elsewhere (22). Steady extensional viscosity, including the η_E^{∞} values, can also be determined in microfluidic cross-slot geometry (37, 39, 104, 105) by analysis of neck-thinning data during drop formation. In such microfluidic experiments, the radius evolution exhibits an exponential decay of the form $R(t) = A \exp(-(\eta_{outer}/\eta_E)\dot{\varepsilon}t)$, where A is a constant (37, 38), η_{outer} is the viscosity of the coflowing outer fluid, and the extensional rate, $\dot{\epsilon}$, is set using an external pump. Even though neither extensional relaxation time nor EC strain increment is obtained from microfluidic measurements, we envision that a comparison of η_F^{∞} values could be insightful, especially for the evaluation of the impact of macromolecular deformation associated with the EC regime present in the radius evolution dataset obtained using the DoS rheometry protocols.

Terminal Extensional Viscosity vs. Relaxation Time and Quantifying Elastocapillary Span. Fig. 4*A* shows a plot of steady, terminal extensional viscosity values for the PEO solutions (two molecular weights) against extensional relaxation time values extracted from DoS rheological measurements. The plot includes two additional datasets obtained by Stelter et al. (59) for semidilute aqueous solutions of two polyacrylamides with different degrees



Fig. 3. Extensional stress, EC strain increment, and extensional viscosity of aqueous PEO solutions. (A) Extensional stress plotted against the Hencky strain shows most datasets look dynamically similar even though polymer concentration varies. The measurements are all at different extensional rates but the same effective Weissenberg number, $Wi = \dot{\epsilon} \lambda_E = 2/3$. (B) The rescaled extensional viscosity as a function of rescaled fluid strain. Strain is rescaled with the strain value at the onset of the finite extensibility or TVEC regime, and transient extensional viscosity is scaled using the η_E^{∞} value determined from TVEC regime, listed in Table 1. (C) EC strain increment, $\Delta \epsilon_{EC}$, and (D) steady, terminal extensional viscosity, η_E^{∞} , as a function of scaled concentration, c/c^* , for the aqueous PEO solutions.

of hydrolysis that makes Praestol 2500 an example of flexible and Praestol 2540 of semiflexible polymers. The spread in data points seen in Fig. 4A is somewhat larger than that shown in datasets by Stelter et al. (59), although the authors mention that their studies were restricted within a narrow concentration regime of $1 < c/c^* < 2$. Fig. 4 shows data for much a broader concentration range $1 < c/c^* < 10$. The differences can be attributed to the contrast in the deformation history between the two devices and to the slight difference in molecular-weight-dependent variation exhibited by the extensional relaxation time and steady-state extensional viscosity, as detailed in a review by McKinley (3). Extensional viscosity of FENE-P chains in ultradilute solutions can be written as $\eta_E^{\infty} \rightarrow 3\eta_s + 2\eta_p L_E^2$, exhibiting a dependence on both shear viscosity as well as the finite extensibility parameter, $L_E^2 = (R_{\text{max}}/R_{us})^2 \propto N_K^{2(1-\nu)}$, defined as the ratio of contour length of a chain to its unstretched length (where v is the solvent quality exponent). Typically, the solvent viscosity is quite small compared with the polymer contribution $\eta_s \ll \eta_p L_E^2$. In the present case, the value of the finite extensibility parameter computed for the flexible PEO chains (using $N_K = 9,280$ for PEO with $M_w = 1 \times 10^6$) is $L_E^2 = 3,840$. In general, as flexible polymers have higher extensibility, their extensional viscosity values are expected to be higher for matched relaxation times, as observed in Fig. 4A and also in the original plot by Stelter et al. (59). We have verified that semidilute PEO solutions formed with three lower molecular weights $(3 \times 10^5, 4 \times 10^5, \text{ and } 6 \times 10^5 \text{ g/mol})$ and two higher molecular weights $(4 \times 10^6 \text{ and } 5 \times 10^6 \text{ g/mol})$ exhibit trends similar to those shown in Figs. 3 and 4, although a shorter relaxation time and iterated stretching respectively pose challenges to the accurate evaluation of both transitions and the TVEC regime (SI Appendix, Supplementary Information). Even though the images of stretched liquid bridges undergoing thinning are not shown in the two papers by Stelter et al. (58, 59), their choices of concentrations and molecular weights are consistent with the restricted range measurable with devices that rely on step strain. Likewise, the shortest relaxation time reported by Stelter et al. (58, 59) is over 30 ms (whereas DoS rheometry allows values at least two orders of

Table 1. Compilation of experimentally determined values of extensional relaxation time, EC span, terminal extensional viscosity, and the Hencky strain at the EC-TVEC transition obtained for the aqueous PEO solutions

<i>M_w</i> , g/mol	c, wt %	η_0 , mPa·s	Oh	Δt_{EC} , s	λ_E , s	η _E ∞, Pa⋅s	ε_{FE}
1 × 10 ⁶	0.75	22	0.11	0.039	0.0068	42	7.5
1×10^{6}	0.5	9.5	0.050	0.0317	0.0049	36	7.9
1×10^{6}	0.3	3.8	0.019	0.015	0.0026	19	7.8
1×10^{6}	0.17	2.5	0.012	0.0154	0.0022	16	7.8
2×10^{6}	1.0	170	0.87	0.171	0.030	225	7.7
2×10^{6}	0.75	80	0.40	0.134	0.026	160	7.6
2×10^{6}	0.6	25	0.13	0.093	0.018	94	7.8
2×10^{6}	0.2	5	0.025	0.048	0.0094	38	7.8

The tabulated values of η_{E}^{∞} and η_{0} imply that relatively high Trouton ratios, $\eta_{E}^{\infty}/\eta_{0} > 10^{3}$, are realized, especially for solutions with Oh < 1.

magnitude lower) and the IC/VC–EC transition is not observed in their radius evolution data (58).

Fig. 4*B* shows the plot of scaled EC span against polymer concentration in the semidilute regime for the two molecular weights of PEO. The scaled EC span, in analogy with EC strain increment and extensional stress in EC regime, shows a nearly constant value of $\Delta t_{EC}/3\lambda_E = 1.9 \pm 0.3$, independent of polymer concentration and molecular weight. Using Eqs. 3 and 4, the scaled EC span can be written in terms of the neck radius at the two transition points, and consequently in terms of the EC strain increment as well in terms of three quantities determined by fitting the radius evolution data, as shown below:

$$\frac{\Delta t_{EC}}{3\lambda_E} = \ln\left(\frac{R_1}{R_2}\right) = \frac{\Delta \varepsilon_{EC}}{2} = \ln\left(\left(\frac{G_E R_0}{2\sigma}\right)^{1/3} \frac{2R_0 \eta_E^{\infty}}{3\sigma \lambda_E}\right).$$
 [7]

The radius at the EC–TVEC transition can be computed as $R_2 = 3\sigma \lambda_E / 2\eta_E^{\infty}$ using the EC balance. An estimate made with the typical values of instrumental parameters and rheological

parameters for aqueous solutions of flexible polymer like PEO yields $R_2 \sim O(10 \ \mu m)$ and the corresponding value falls in proportion to surface tension, making visualization EC-TVEC transition or TVEC region harder for organic solvents. The key aspect that emerges from Fig. 4 and Eq. 7 is that the values of η_E^{∞} as well as Δt_{EC} and $\Delta \varepsilon_{EC}$ (also included in Table 1) are all proportional to extensional relaxation time and exhibit the same concentration-dependent response as is exhibited by λ_E values. Our results show that lower concentrations and molecular weights and lower extensibility of macromolecules lead to shorter relaxation time and EC span values, resulting in shorter pinch-off times, and are therefore more suitable for designing complex fluids formulations for printing, jetting, and spraying applications. In contrast, the spinnability and effective stickiness of polymer solutions increase with corresponding increase in the overall pinch-off time or filament lifespan and extensional viscosity values. The concentrationand molecular-weight-dependent variation in the values of extensional viscosity (η_E and η_E^{∞} , EC span, $\Delta t_{EC}/\lambda_E$, and EC strain, $\Delta \varepsilon_{EC}$, are directly correlated with the corresponding variation in extensional relaxation time, λ_E).

Summary. In the present study we show that the DoS rheometry protocols allow the characterization of transition from initial IC (or VC for higher-viscosity fluids) regime to the EC regime that is often masked or absent in the radius evolution data obtained from CaBER measurements. Likewise, we show that the DoS rheometry protocols also allow the visualization and analysis of the finite extensibility or TVEC regime, as well as the EC-TVEC transition. It is well established that the visualization and quantitative analysis of neck-thinning dynamics can be used for contrasting the influence of different polymers and other additives and also for quantifying the magnitude and behavior of governing stresses and underlying flow kinematics (3). In addition to the three conventional extensional rheological measures determined from analysis of radius evolution data, namely the transient extensional viscosity η_E , the steady, terminal extensional viscosity η_E^{∞} , and the extensional relaxation time λ_E extracted from neck-thinning dynamics we introduce and quantify three



Fig. 4. Steady-state extensional viscosity as a function of extensional relaxation time and concentration-dependent variation in EC span scaled with extensional relaxation time. (*A*) Terminal, steady extensional viscosity values extracted from the linear fit to the TVEC data are plotted as ordinate, whereas abscissa are the corresponding values of extensional relaxation time extracted from the EC fit. The dotted lines correspond to the response for flexible and semiflexible polymer solutions as was reported by Stelter et al. (59) and data for aqueous polyacrylamide (PAM or Praestol) solutions are extracted from a plot in Stelter et al. (59) (*B*) Dimensionless EC time $\Delta t_{EC}/(3\lambda_E)$ as a function of dimensionless concentration for aqueous PEO solutions seems to all display a concentration-independent mean value $\Delta t_{EC}/(3\lambda_E) = 1.9 \pm 0.3$.

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 $(\tau_E = \eta_F \dot{\epsilon})$ with Hencky strain show a nearly concentrationindependent 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

- 1. Middleman S (1965) Stability of a viscoelastic jet. Chem Eng Sci 20:1037–1040.
- 2. Eggers J (1997) Nonlinear dynamics and breakup of free-surface flows. *Rev Mod Phys* 69:865–929.
- McKinley GH (2005) Visco-elasto-capillary thinning and break-up of complex fluids. *Rheology Reviews* 2005:1–48.
- Yarin AL (1993) Free Liquid Jets and Films: Hydrodynamics and Rheology (Longman, New York).
- Bazilevskii AV, Voronkov SI, Entov VM, Rozhkov AN (1981) Orientational effects in the decomposition of streams and strands of diluted polymer solutions. Sov Phys Dokl 26:333–335.
- Entov VM, Yarin AL (1984) Influence of elastic stresses on the capillary breakup of jets of dilute polymer solutions. *Fluid Dyn* 19:21–29.
- Bousfield DW, Keunings R, Marrucci G, Denn MM (1986) Nonlinear analysis of the surface tension driven breakup of viscoelastic filaments. J Non Newt Fluid Mech 21: 79–97.
- 8. Christanti Y, Walker LM (2001) Surface tension driven jet break up of strainhardening polymer solutions. J Non Newt Fluid Mech 100:9–26.
- Christanti Y, Walker LM (2002) Effect of fluid relaxation time of dilute polymer solutions on jet breakup due to a forced disturbance. J Rheol (NYNY) 46:733–748.
- Ardekani A, Sharma V, McKinley GH (2010) Dynamics of bead formation, filament thinning and breakup of weakly viscoelastic jets. J Fluid Mech 665:46–56.
- Sharma V, et al. (2015) The rheology of aqueous solutions of ethyl hydroxy-ethyl cellulose (EHEC) and its hydrophobically modified analogue (hmEHEC): Extensional flow response in capillary break-up, jetting (ROJER) and in a cross-slot extensional rheometer. Soft Matter 11:3251–3270.
- Keshavarz B, et al. (2015) Studying the effects of elongational properties on atomization of weakly viscoelastic solutions using Rayleigh Ohnesorge Jetting Extensional Rheometry (ROJER). J Non Newt Fluid Mech 222:171–189.
- Mathues W, Formenti S, McIlroy C, Harlen OG, Clasen C (2018) CaBER vs ROJER-Different time scales for the thinning of a weakly elastic jet. J Rheol (NYNY) 62: 1135–1153.
- Tirtaatmadja V, McKinley GH, Cooper-White JJ (2006) Drop formation and breakup of low viscosity elastic fluids: Effects of molecular weight and concentration. *Phys Fluids* 18:043101.
- Wagner C, Amarouchene Y, Bonn D, Eggers J (2005) Droplet detachment and satellite bead formation in viscoelastic fluids. *Phys Rev Lett* 95:164504.

 $c^*[\eta] \approx 1$ 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 $K = 1.25 \times 10^{-2} \text{mL/g}$ 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 $D_0 = 1.270$ 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/D₀, 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 \times 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 concentrationdependent extensional relaxation time of neutral and charged polymer solutions can be found in our previous publications (22-26).

ACKNOWLEDGMENTS. V.S. and J.D. thank Cynthia Jameson (University of Illinois at Chicago), Amanda Marciel (Rice University), Samanvaya Srivastava (University of California, Los Angeles), and students in the Optics, Dynamics, Elasticity and Self-Assembly laboratory for close reading of the manuscript and their questions and comments. V.S. thanks the College of Engineering and the Department of Chemical Engineering, University of Illinois at Chicago, for support.

- sity of
- Amarouchene Y, Bonn D, Meunier J, Kellay H (2001) Inhibition of the finite-time singularity during droplet fission of a polymeric fluid. *Phys Rev Lett* 86:3558–3561.
- Ambravaneswaran B, Wilkes ED, Basaran OA (2002) Drop formation from a capillary tube: Comparison of one-dimensional and two-dimensional analyses and occurrence of satellite drops. *Phys Fluids* 14:2606–2621.
- Castrejón-Pita JR, et al. (2015) Plethora of transitions during breakup of liquid filaments. Proc Natl Acad Sci USA 112:4582–4587.
- Dinic J, Sharma V (2019) Computational analysis of self-similar capillary-driven thinning and pinch-off dynamics during dripping using the volume-of-fluid method. *Phys Fluids* 31:021211.
- 20. Deblais A, et al. (2018) Viscous effects on inertial drop formation. *Phys Rev Lett* 121: 254501.
- Clasen C, Phillips PM, Palangetic L (2012) Dispensing of rheologically complex fluids: The map of misery. AIChE J. 58:3242–3255.
- Dinic J, Biagioli M, Sharma V (2017) Pinch-off dynamics and extensional relaxation times of intrinsically semi-dilute polymer solutions characterized by dripping-ontosubstrate rheometry. J Polym Sci B Polym Phys 55:1692–1704.
- Dinic J, Jimenez LN, Sharma V (2017) Pinch-off dynamics and dripping-ontosubstrate (DoS) rheometry of complex fluids. Lab Chip 17:460–473.
- Dinic J, Zhang Y, Jimenez LN, Sharma V (2015) Extensional relaxation times of dilute, aqueous polymer solutions. ACS Macro Lett 4:804–808.
- Jimenez LN, Dinic J, Parsi N, Sharma V (2018) Extensional relaxation time, pinch-off dynamics and printability of semi-dilute polyelectrolyte solutions. *Macromolecules* 51:5191–5208.
- Hsiao KW, Dinic J, Ren Y, Sharma V, Schroeder CM (2017) Passive non-linear microrheology for determining extensional viscosity. *Phys Fluids* 29:121603.
- Clasen C, et al. (2006) How dilute are dilute solutions in extensional flows? J Rheol (NYNY) 50:849–881.
- Basaran OA, Gao H, Bhat PP (2013) Nonstandard inkjets. Annu Rev Fluid Mech 45: 85–113.
- 29. Kumar S (2014) Liquid transfer in printing processes: Liquid bridges with moving contact lines. Annu Rev Fluid Mech 47:67–94.
- Fernando RH, Lundberg DJ, Glass JE (1989) Importance of elongational flows in the performance of water-borne formulations. Adv Chem 223:245–259.
- Ashgriz N, ed (2011) Handbook of Atomization and Sprays: Theory and Applications (Springer, New York).

- Thompson JC, Rothstein JP (2007) The atomization of viscoelastic fluids in flat-fan and hollow-cone spray nozzles. J Non-Newt Fluid Mech 147:11–22.
- Ramaswamy S, Leal LG (1999) The deformation of a viscoelastic drop subjected to steady uniaxial extensional flow of a Newtonian fluid. J Non Newt Fluid Mech 85: 127–163.
- 34. Stone HA (1994) Dynamics of drop deformation and breakup in viscous fluids. Annu Rev Fluid Mech 26:65–102.
- Christopher GF, Anna SL (2007) Microfluidic methods for generating continuous droplet streams. J Phys D Appl Phys 40:R319–R336.
- Christopher GF, Anna SL (2009) Passive breakup of viscoelastic droplets and filament self-thinning at a microfluidic T-junction. J Rheol (NYNY) 53:663–683.
- Arratia PE, Gollub JP, Durian DJ (2008) Polymeric filament thinning and breakup in microchannels. Phys Rev E Stat Nonlin Soft Matter Phys 77:036309.
- Juarez G, Arratia PE (2011) Extensional rheology of DNA suspensions in microfluidic devices. Soft Matter 7:9444–9452.
- Ingremeau F, Kellay H (2013) Stretching polymers in droplet-pinch-off experiments. Phys. Rev. X 3:041002
- Bhat PP, et al. (2010) Formation of beads-on-a-string structures during break-up of viscoelastic filaments. Nat Phys 6:625–631.
- Haward SJ, Sharma V, Odell JA (2011) Extensional opto-rheometry with biofluids and ultra-dilute polymer solutions. Soft Matter 7:9908–9921.
- Gaume L, Forterre Y (2007) A viscoelastic deadly fluid in carnivorous pitcher plants. PLoS One 2:e1185.
- Erni P, Varagnat M, Clasen C, Crest J, McKinley GH (2011) Microrheometry of subnanolitre biopolymer samples: Non-Newtonian flow phenomena of carnivorous plant mucilage. Soft Matter 7:10889–10898.
- Palangetic L, et al. (2014) Dispersity and spinnability: Why highly polydisperse polymer solutions are desirable for electrospinning. *Polymer (Guildf)* 55:4920–4931.
- Haward SJ, Sharma V, Butts CP, McKinley GH, Rahatekar SS (2012) Shear and extensional rheology of cellulose/ionic liquid solutions. *Biomacromolecules* 13:1688–1699.
- Fang Y, Dulaney AD, Gadley J, Maia JM, Ellison CJ (2015) Manipulating characteristic timescales and fiber morphology in simultaneous centrifugal spinning and photopolymerization. *Polymer (Guildf)* 73:42–51.
- Nguyen TQ, Kausch HH (1999) Flexible Polymer Chains in Elongational Flow: Theory and Experiment (Springer, Berlin).
- Schroeder CM (2018) Single polymer dynamics for molecular rheology. J Rheol (NYNY) 62:371–403.
- Prabhakar R, Gadkari S, Gopesh T, Shaw MJ (2016) Influence of stretching induced self-concentration and self-dilution on coil-stretch hysteresis and capillary thinning of unentangled polymer solutions. J Rheol (NYNY) 60:345–366.
- Prabhakar R, Sasmal C, Nguyen DA, Sridhar T, Prakash JR (2017) Effect of stretchinginduced changes in hydrodynamic screening on coil-stretch hysteresis of unentangled polymer solutions. *Phys Rev Fluids* 2:011301.
- Schroeder CM, Babcock HP, Shaqfeh ESG, Chu S (2003) Observation of polymer conformation hysteresis in extensional flow. *Science* 301:1515–1519.
- Schroeder CM, Shaqfeh ESG, Chu S (2004) Effect of hydrodynamic interactions on DNA dynamics in extensional flow: Simulation and single molecule experiment. *Macromolecules* 37:9242–9256.
- Larson RG (2005) The rheology of dilute solutions of flexible polymers: Progress and problems. J Rheol (NYNY) 49:1–70.
- Larson RG, Magda JJ (1989) Coil-stretch transitions in mixed shear and extensional flows of dilute polymer solutions. *Macromolecules* 22:3004–3010.
- Hsieh CC, Larson RG (2005) Prediction of coil-stretch hysteresis for dilute polystyrene molecules in extensional flow. J Rheol (NYNY) 49:1081–1089.
- de Gennes PG (1974) Coil-stretch transition of dilute flexible polymers under ultrahigh velocity gradients. J Chem Phys 60:5030–5042.
- 57. Entov VM, Hinch EJ (1997) Effect of a spectrum of relaxation times on the capillary thinning of a filament of elastic liquid. J Non Newt Fluid Mech 72:31–54.
- Stelter M, Brenn G, Yarin AL, Singh RP, Durst F (2000) Validation and application of a novel elongational device for polymer solutions. J Rheol (NYNY) 44:595–616.
- Stelter M, Brenn G, Yarin AL, Singh RP, Durst F (2002) Investigation of the elongational behavior of polymer solutions by means of an elongational rheometer. *J Rheol (NYNY)* 46:507–527.
- Oliveira MSN, McKinley GH (2005) Iterated stretching and multiple beads-on-a-string phenomena in dilute solutions of highly extensible flexible polymers. *Phys Fluids* 17: 071704.
- Oliveira MSN, Yeh R, McKinley GH (2006) Iterated stretching, extensional rheology and formation of beads-on-a-string structures in polymer solutions. J Non Newt Fluid Mech 137:137–148.
- Plog J, Kulicke W, Clasen C (2005) Influence of the molar mass distribution on the elongational behaviour of polymer solutions in capillary breakup. *Appl Rheol* 15: 28–37.
- Yaoita T, et al. (2011) Primitive chain network simulation of elongational flows of entangled linear chains: Role of finite chain extensibility. *Macromolecules* 44: 9675–9682.
- Odell JA, Muller AJ, Narh KA, Keller A (1990) Degradation of polymer solutions in extensional flows. *Macromolecules* 23:3092–3103.
- Islam MT, Vanapalli SA, Solomon MJ (2004) Inertial effects on polymer chain scission in planar elongational cross-slot flow. *Macromolecules* 37:1023–1030.
- Caruso MM, et al. (2009) Mechanically-induced chemical changes in polymeric materials. Chem Rev 109:5755–5798.
- Day RF, Hinch EJ, Lister JR (1998) Self-similar capillary pinchoff of an inviscid fluid. Phys Rev Lett 80:704–707.

- Eggers J, Fontelos MA (2015) Singularities: Formation, Structure, and Propagation (Cambridge Univ Press, Cambridge, UK).
- 69. Papageorgiou DT (1995) On the breakup of viscous liquid threads. *Phys Fluids* 7: 1529–1544.
- Bazilevskii AV, Entov VM, Rozhkov AN (2001) Breakup of an Oldroyd liquid bridge as a method for testing the rheological properties of polymer solutions. *Polym Sci A* 43: 716–726.
- Bazilevsky A, Entov V, Rozhkov A (1990) Liquid filament microrheometer and some of its applications. *Third European Rheology Conference and Golden Jubilee Meeting of the British Society of Rheology* (Elsevier, Amsterdam), pp 41–43.
- Bazilevsky AV, Entov VM, Rozhkov AN (2011) Breakup of a liquid bridge as a method of rheological testing of biological fluids. *Fluid Dyn* 46:613–622.
- Anna SL, McKinley GH (2001) Elasto-capillary thinning and breakup of model elastic liquids. J Rheol (NYNY) 45:115–138.
- Rodd LE, Scott TP, Cooper-White JJ, McKinley GH (2005) Capillary break-up rheometry of low-viscosity elastic fluids. Appl Rheol 15:12–27.
- Campo-Deano L, Clasen C (2010) The slow retraction method (SRM) for the determination of ultra-short relaxation times in capillary breakup extensional rheometry experiments. J Non Newt Fluid Mech 165:1688–1699.
- Vadillo DC, Mathues W, Clasen C (2012) Microsecond relaxation processes in shear and extensional flows of weakly elastic polymer solutions. *Rheol Acta* 51:755–769.
- Arnolds O, Buggisch H, Sachsenheimer D, Willenbacher N (2010) Capillary breakup extensional rheometry (CaBER) on semi-dilute and concentrated polyethyleneoxide (PEO) solutions. *Rheol Acta* 49:1207–1217.
- Clasen C (2010) Capillary breakup extensional rheometry of semi-dilute polymer solutions. Korea Australia Rheol J 22:331–338.
- Clasen C, Eggers J, Fontelos MA, Li J, McKinley GH (2006) The beads-on-string structure of viscoelastic threads. J Fluid Mech 556:283–308.
- Marshall KA, Liedtke AM, Todt AH, Walker TW (2017) Extensional rheometry with a handheld mobile device. *Exp Fluids* 6:1–9.
- Sur S, Rothstein J (2018) Drop breakup dynamics of dilute polymer solutions: Effect of molecular weight, concentration, and viscosity. J Rheol (NYNY) 62:1245–1259.
- Zhang YR, Muller SJ (2018) Unsteady sedimentation of a sphere in wormlike micellar fluids. *Phys Rev Fluids* 3:043301.
- Walter AV, Jimenez LN, Dinic J, Sharma V, Erk KA (2019) Effect of salt valency and concentration on shear and extensional rheology of aqueous polyelectrolyte solutions for enhanced oil recovery. *Rheol Acta* 2019:1–13.
- Omidvar R, Wu S, Mohammadigoushki H (2019) Detecting wormlike micellar microstructure using extensional rheology. J Rheol (NYNY) 63:33–44.
- Chen AU, Notz PK, Basaran OA (2002) Computational and experimental analysis of pinch-off and scaling. *Phys Rev Lett* 88:174501.
- 86. McKinley GH, Renardy M (2011) Wolfgang von Ohnesorge. Phys Fluids 23:127101.
- Renardy M (1995) A numerical study of the asymptotic evolution and breakup of Newtonian and viscoelastic jets. J Non Newt Fluid Mech 59:267–282.
- Wagner C, Bourouiba L, McKinley GH (2015) An analytic solution for capillary thinning and breakup of FENE-P fluids. J Non Newt Fluid Mech 218:53–61.
- Zhou J, Doi M (2018) Dynamics of viscoelastic filaments based on Onsager principle. *Phys Rev Fluids* 3:084004.
- Fontelos MA, Li J (2004) On the evolution and rupture of filaments in Giesekus and FENE models. J Non Newt Fluid Mech 118:1–16.
- Fuller GG, Leal LG (1981) Flow birefringence of concentrated polymer solutions in two dimensional flows. J Polym Sci B Polym Phys 19:557–587.
- Fuller GG, Leal LG (1980) Flow birefringence of dilute polymer solutions in twodimensional flows. *Rheol Acta* 19:580–600.
- Ng RCY, Leal LG (1993) Concentration effects on birefringence and flow modification of semidilute polymer solutions in extensional flows. J Rheol (NYNY) 37: 443–468.
- Pope DP, Keller A (1977) Alignment of macromolecules in solution by elongational flow; a study of the effect of pure shear in a four roll mill. *Colloid Polym Sci* 255: 633–643.
- Müller AJ, Odell JA, Keller A (1988) Elongational flow and rheology of monodisperse polymers in solution. J Non Newt Fluid Mech 30:99–118.
- Tatham JP, et al. (1995) Extensional behavior of hydropxypropyl guar solutions– Optical rheometry in opposed jets and flow through porous media. J Rheol (NYNY) 39:961–986.
- Hudson SD, et al. (2004) Microfluidic analog of the four-roll mill. Appl Phys Lett 85: 335–337.
- 98. Fuller GG (1995) Optical Rheometry of Complex Fluids (Oxford Univ Press, New York).
- 99. Treloar LRG (1975) The Physics of Rubber Elasticity (Oxford Univ Press, Oxford).
- Kuhn W, Grün F (1942) Beziehungen zwischen elastischen Konstanten und Dehnungsdoppelbrechung hochelastischer Stoffe. Kolloid Zeitschrift 101:248–271.
- Peterlin A (1966) Hydrodynamics of macromolecules in a velocity field with longitudinal gradient. J Polym Sci B 4:287–291.
- Peterlin A (1961) Streaming birefringence of soft linear macromolecules with finite chain length. *Polymer (Guildf)* 2:257–264.
- 103. Tropea C, Yarin AL (2007) Springer Handbook of Experimental Fluid Mechanics (Springer, New York).
- 104. Arratia PE, Cramer LA, Gollub JP, Durian DJ (2009) The effects of polymer molecular weight on filament thinning and drop breakup in microchannels. New J Phys 11: 115006.
- 105. Sachdev S, Muralidharan A, Boukany PE (2016) Molecular processes leading to "necking" in extensional flow of polymer solutions: Using microfluidics and single DNA imaging. *Macromolecules* 49:9578–9585.
- 106. Mark JE (2009) Polymer Data Handbook (Oxford Univ Press, New York).