

Effects of Polydispersity and Concentration on Elastocapillary Thinning of Dilute Polymer Solutions

Vincenzo Calabrese[✉], Amy Q. Shen[✉], and Simon J. Haward[✉]

Okinawa Institute of Science and Technology Graduate University, Onna-son, Okinawa, 904-0495, Japan



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The self-thinning of liquid bridges under the action of capillarity occurs in widespread processes like jetting, dripping, and spraying and gives rise to a strong extensional flow capable of stretching dissolved polymers. If the resulting elastic stress exceeds the viscous stress, an exponential “elastocapillary” (EC) thinning regime arises, yielding a timescale τ_{EC} that is commonly considered equivalent to the longest relaxation time of the polymer λ . A long-standing question is why τ_{EC} depends strongly on the polymer concentration, even at high dilutions where λ should be constant in theory. To date, this is understood in terms of intermolecular interactions that arise due to “self-concentration” effects as polymers stretch. However, λ depends on the polymer molecular weight M , and we show how the concentration dependence of τ_{EC} can be explained by considering the molecular weight distribution (MWD) inherent in real polymer samples, without the need to invoke self-concentration. We demonstrate this by blending low- M and high- M polymer samples with narrow MWDs at dilute concentrations and in different proportions and by measuring τ_{EC} for each blend in capillary thinning experiments. Through a simple model that qualitatively reproduces the experimental results, we show how elastic stresses generated by the polymer build up prior to the EC regime due to the sequential stretching of progressively decreasing molecular weight species in the MWD. Since the elastic stress generated by each species depends on its concentration, the fraction of the MWD that is required to stretch in order to induce the EC regime depends on the total polymer concentration c in the solution. For higher c , the EC regime is induced by stretching of a higher- M (longer λ) fraction of the MWD and results in a longer measurement of τ_{EC} . Our results have significant implications for the application of capillary thinning measurements to extensional rheometry, for the interpretation of such measurements, and for the understanding of elastocapillary thinning dynamics in general.

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I. INTRODUCTION

The self-thinning and breakup of liquid bridges under the action of capillarity is ubiquitous in widespread natural and industrial processes involving both simple Newtonian fluids (like water) and more complex non-Newtonian fluids (e.g., solutions of proteins, DNA, or synthetic polymers). Important examples include the fluid breakup and fragmentation processes in spraying and coating applications [1,2], dripping [3,4], fiber spinning [5,6], ink-jet printing [7–9], additive manufacturing [10], misting, and aerosolization (including during sneezing and speech) [11–14]. In cases where inertia can be neglected, the capillary-driven thinning of Newtonian liquid bridges is controlled by a viscocapillary (VC) stress balance and is linear in time

[15,16]. For polymer solutions, the squeezing of the fluid neck by the capillary pressure can induce additional elastic stresses associated with the stretching of polymers, resulting in a regime of exponential thinning controlled by an elastocapillary (EC) stress balance [17–19]. Measurements of the rate of exponential thinning in the EC regime are widely used among the complex fluids, soft matter, and polymer science communities to extract rheological properties, e.g., “relaxation times,” of polymeric fluids [18–30]. However, several recent studies [31–35] have raised concerns about the accuracy and validity of these measurements under certain conditions.

Here, we are particularly concerned with the experimental observation that characteristic timescales τ_{EC} measured in the EC regime depend on the concentration c of polymer in solution. This is observed even well below the equilibrium polymer overlap concentration c^* where interpolymer interactions should be negligible and the relaxation time λ should be independent of c [19,25,26,29,36–38]. In a 2005 review article, this unexpected concentration dependence of τ_{EC} was cited as an “outstanding remaining challenge” to

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the understanding of elastocapillary thinning dynamics [36]. Since then, it has become accepted that intermolecular hydrodynamic interactions become important as coiled polymer chains unravel and stretch in the thinning fluid neck, affecting the determination of τ_{EC} even if the fluid would normally be considered dilute at equilibrium. The increasing dimension of the coil as the polymer unravels is understood as leading to an effectively reduced overlap concentration, a so-called “self-concentration” effect. The implication is that, in order to obtain a concentration-independent value for τ_{EC} , the fluid must be “ultradilute” at equilibrium, such that intermolecular interactions remain negligible even when the polymer becomes highly stretched [19,39–42]. Conformation-dependent interchain hydrodynamic interactions are complex, however, and there have been recent counterarguments to the concept of self-concentration due to polymer chain stretching [43–45].

Although intermolecular interactions clearly influence polymeric relaxation times beyond a certain concentration (normally considered to be c^*), in this paper, we consider the role of a polydisperse molecular weight distribution (MWD) and its possible influence on the determination of τ_{EC} . Polydispersity in molecular weight results in a wide spectrum of relaxation times, significantly affecting the mechanical and rheological properties of polymers [46–48]. Experimental studies (e.g., Refs. [29,49,50]) clearly show that polydispersity influences EC thinning dynamics. It has also been shown how the addition of a high molecular weight polymer to a lower molecular weight solution (making a bimodal MWD) can stabilize threads of elastic fluids, retarding their breakup in fiber-spinning applications [51,52]. But perhaps the most influential interpretation of the role of MWD on the EC thinning of polymer solutions stems from an early theoretical analysis of a multimode finitely extensible nonlinear elastic (FENE) fluid [17]. From this analysis, it is widely thought that the characteristic time τ_{EC} corresponds to the relaxation time of the longest, or highest molecular weight, polymers in the sample.

Here, we propose that, in fact, MWD is a plausible explanation for the concentration dependence of τ_{EC} at high dilutions, since the observation of an EC thinning regime depends on the generation of sufficient elastic stress by the stretching of polymer, which is itself concentration dependent [19]. Given a polymer sample with a distribution of molecular weights (two examples in Fig. 1), we argue that below a certain concentration there will be an insufficient number of molecules in the high- M tail to generate the required elastic stress. In such a case, we imagine a scenario in which a more abundant lower- M portion of the MWD may dominate the EC response of the fluid. Since the relaxation time depends on the molecular weight M of the polymer (as $\lambda \sim M^{3/2}$ for an ideal system), we propose that an interplay between the MWD and the polymer

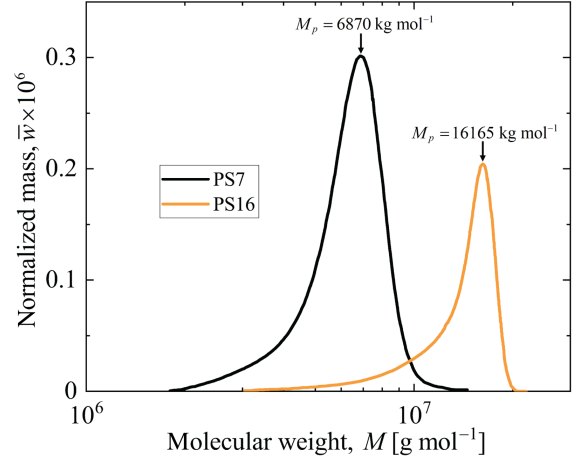


FIG. 1. Normalized molecular weight distributions for the atactic polystyrene samples PS7 and PS16, from GPC analysis provided by the polymer supplier.

concentration dictates the determination of the elastocapillary timescale τ_{EC} .

We elucidate the interplay between MWD and c experimentally by employing two polymer samples with narrow and well-defined MWDs and distinct peak molecular weights M_p (Fig. 1). We measure τ_{EC} for each of the samples individually over a range of concentration and also for blends of the two samples, where the concentration of the low- M_p component remains fixed and that of the high- M_p component is progressively increased. For low concentrations of the high- M_p component, the EC response is dominated by the low- M_p component in the blend. However, if the concentration of the high- M_p component in the blend is sufficient, then it dominates the EC response and the low- M_p component plays no apparent role. By assuming the progressive stretching of decreasing molecular weight species in the MWD and performing a backward summation of the elastic stress contributions arising from each fully stretched molecular weight, the experimental results are qualitatively reproduced. Our findings are of significance to the application of capillary thinning techniques to extensional rheometry, to the interpretation of such measurements, and also to the understanding of elastocapillary thinning dynamics in general.

II. EXPERIMENTAL METHODS

A. Materials

Two samples of high molecular weight and low polydispersity atactic polystyrene (PS) sourced from Agilent Technologies Inc. (Santa Clara, CA) are used in the experiments. One of the samples (labeled PS7) has a peak molecular weight $M_p = 6.87 \times 10^6 \text{ g mol}^{-1}$, with weight-averaged and number-averaged molecular weights of $M_w = 6.20 \times 10^6 \text{ g mol}^{-1}$ and $M_n = 5.67 \times 10^6 \text{ g mol}^{-1}$, respectively (polydispersity index, $\text{PDI} = M_w/M_n = 1.09$).

The other sample (labeled PS16) has $M_p = 16.17 \times 10^6 \text{ g mol}^{-1}$, $M_w = 14.48 \times 10^6 \text{ g mol}^{-1}$, and $M_n = 13.48 \times 10^6 \text{ g mol}^{-1}$ (PDI = 1.07). The normalized MWDs of the two samples, obtained via gel permeation chromatography (GPC) characterization provided by the polymer supplier, are shown in Fig. 1. The samples have narrow distributions with clearly distinct peaks but which overlap in a range of $3 \times 10^6 \lesssim M \lesssim 14.5 \times 10^6 \text{ g mol}^{-1}$.

Stock solutions of PS7 and PS16 are prepared at concentrations of $c_{\text{PS7}} = 15000 \text{ ppm}$ and $c_{\text{PS16}} = 10000 \text{ ppm}$ (by weight), respectively, in the solvent dioctyl phthalate (DOP) using the intermediate solvent method, as described in Ref. [53].

Dioctyl phthalate is a moderately viscous ($\eta_s \approx 57 \text{ mPa s}$) and nonvolatile θ solvent for polystyrene at $T = 295 \text{ K}$ (i.e., close to laboratory temperature) [54]. Equilibrium chain parameters for PS in DOP can be estimated based on an ideal 3D random walk of Kuhn segments of length $b = C_\infty \ell$ and number of steps $N = n/C_\infty$ (neglecting bond angles), where $C_\infty = 9.7$ is the characteristic ratio, $\ell = 0.154 \text{ nm}$ is the C—C bond length, $n = 2M/m$ is the number of C—C bonds in a PS molecule of molar mass M , and $m = 104 \text{ g mol}^{-1}$ is the molar mass of the styrene monomer [55]. The equilibrium end-to-end length is $\langle R_0 \rangle = b\sqrt{N}$, and radius of gyration is $R_g = \langle R_0 \rangle / \sqrt{6}$. The overlap concentration can be estimated based on cubic packing of polymer coils as $c^* = M/(8N_A R_g^3)$ [56]. The contour length of the chain is given by $l_c = n\ell (\equiv Nb)$, and the polymer chain extensibility can be estimated as:

$$L = l_c / \langle R_0 \rangle. \quad (1)$$

Finally, the Zimm relaxation time for the ideal chain can be estimated as [57,58]:

$$\lambda_Z = \frac{1}{2\sqrt{3}\pi} \frac{\eta_s R_g^3}{k_B T}, \quad (2)$$

where k_B is the Boltzmann constant and T is the absolute temperature.

In order to observe a transition from Newtonian-like thinning to an exponential EC regime in a capillary thinning experiment, the elastic stress due to the stretching polymer must exceed the viscous stress due to the Newtonian solvent. Clasen *et al.* [19] have derived an expression for the minimum concentration $c_{\min}$ of polymer which, when fully stretched, would provide sufficient elastic stress to induce an observable EC regime:

$$c_{\min} = \frac{3}{2} \frac{M \eta_s}{N_A k_B T \lambda_Z L^2}, \quad (3)$$

where N_A is the Avogadro constant.

Campo-Deaño and Clasen [20] have derived another concentration criterion for EC thinning (termed c_{low}) describing the concentration of polymer required to induce an EC regime in the early stages of stretching, well before the onset of finite extensibility effects (a supposed requirement for the extrapolation of $\tau_{\text{EC}} \equiv \lambda$ according to the prediction of the Oldroyd-B model; see Sec. II B):

$$c_{\text{low}} = \frac{1}{2.46} \frac{M}{N_A k_B T} \left(\frac{\gamma^2 \rho}{\lambda_Z^2} \right)^{1/3} \frac{1}{L^{3/2}}, \quad (4)$$

where γ and ρ are the surface tension and density of the fluid, respectively. For DOP at 25°C , $\gamma \approx 0.031 \text{ N m}^{-1}$ and $\rho \approx 981 \text{ kg m}^{-3}$ [59].

More recently, Dinic and Sharma [42] introduced a “stretched overlap concentration” c_s^* , which considers fully stretched polymers as rodlike molecules and computes a corresponding overlap concentration based on the theory of Doi and Edwards [60]:

$$c_s^* \approx \left(\frac{Nb}{dL^3} \right) c^*, \quad (5)$$

where d is the diameter of a Kuhn segment and for PS $d \approx 1 \text{ nm}$ [61]. The value c_s^* is proposed as an upper limit for ultradilution, above which concentration dependency of τ_{EC} is expected based on currently accepted arguments [42].

The values of all the molecular parameters and concentration criteria described above are presented for the PS7 and PS16 polymer samples (evaluated for $M = M_p$) in Table I. The $c_{\min}$, c_{low} , and c_s^* criteria are discussed in more detail later in the text.

Solutions of PS7 and PS16 are prepared at test concentrations $c_{\text{PS7}} = [200, 500, 1000] \text{ ppm}$ and $c_{\text{PS16}} = [5, 10, 20, 50, 100, 200] \text{ ppm}$ by progressive dilution of the stock solutions with additional DOP. The diluted fluids are placed on a roller mixer turning at 0.5 Hz until they are completely homogeneous (at least 24 h) and subsequently left to stand and equilibrate for a further 24 h prior to performing characterization tests or experimentation. As clear from the data provided in Table I, the test concentrations of both PS7 and PS16 are all well below c^* and, therefore, can be considered dilute. Note also that all values of c_{PS7} are significantly greater than either $c_{\min, \text{PS7}}$ or $c_{\text{low}, \text{PS7}}$,

TABLE I. Molecular parameters of the polystyrene samples under θ -solvent conditions in DOP solution, evaluated for $M = M_p$.

Polymer sample	M_p (kg mol^{-1})	M_w (kg mol^{-1})	PDI	N	b (nm)	$\langle R_0 \rangle$ (nm)	R_g (nm)	l_c (μm)	L	λ_Z (ms)	c^* (ppm)	$c_{\min}$ (ppm)	c_{low} (ppm)	c_s^* (ppm)
PS7	6870	6200	1.09	13 600	1.49	174	71.2	20.3	117	1.03	3960	17.4	84	50
PS16	16 165	14 480	1.07	32 000	1.49	267	109	47.9	179	3.73	2580	4.8	44	21

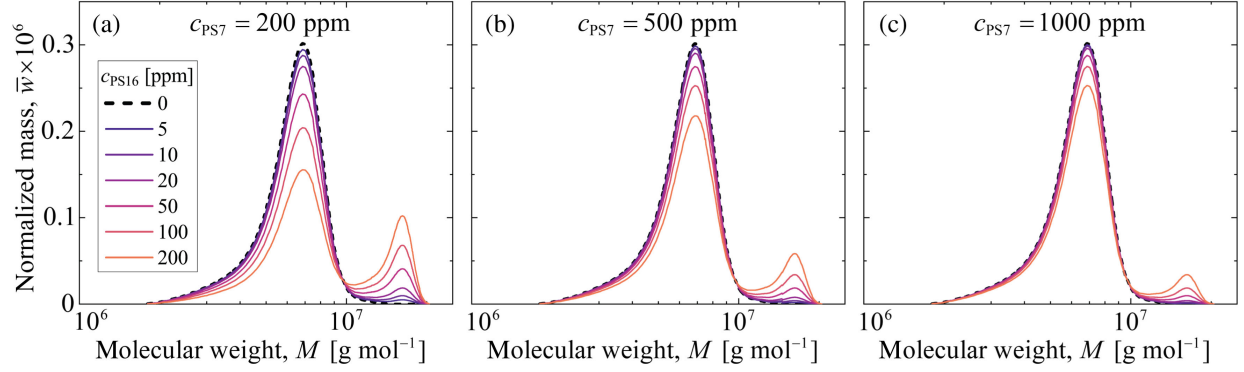


FIG. 2. Normalized MWDs for blends of PS7 and PS16 at PS7 concentrations of (a) $c_{\text{PS7}} = 200$ ppm, (b) $c_{\text{PS7}} = 500$ ppm, and (c) $c_{\text{PS7}} = 1000$ ppm and at the PS16 concentrations c_{PS16} indicated in the legend.

so that at the tested concentrations all of the PS7 solutions could be expected to elicit a clear EC response during capillary thinning. On the other hand, for the PS16 solutions, as the concentration $c_{\text{PS16}} \rightarrow c_{\text{min,PS16}} < c_{\text{low,PS16}}$, a diminishing EC response might be expected.

Blends at each concentration of c_{PS7} and c_{PS16} (total concentration $c = c_{\text{PS7}} + c_{\text{PS16}}$) are prepared by appropriate mixing of PS7 and PS16 solutions and the addition of further DOP, if necessary. As for the pure PS7 and PS16 test solutions, following the preparation of a blend, the fluid is left on a roller mixer turning at 0.5 Hz until homogeneous and then allowed to stand for a further 24 h prior to experimentation. Overlap concentrations for the blends can be estimated as $c^* \approx (c_{\text{PS7}} \times c_{\text{PS7}}^* + c_{\text{PS16}} \times c_{\text{PS16}}^*)/c$. For the most concentrated mixture with $c_{\text{PS7}} = 1000$ ppm and $c_{\text{PS16}} = 200$ ppm, the overlap concentration is $c^* \approx 3730$ ppm (i.e., $c/c^* \approx 0.3$), indicating that all of the blended fluids remain in the dilute regime.

Combining the normalized MWDs shown in Fig. 1 in appropriate ratios enables computation of the MWD of the polymer contained in each of the blended fluids. Normalized MWDs for the blends are shown in Fig. 2. For each concentration of PS7, the addition of a relatively small amount of PS16 essentially contributes a high- M shoulder on the PS7 MWD. However, with increasing c_{PS16} , a clearly bimodal MWD emerges. It is important to note for interpretation of the results to be presented later that, due to the overlap between the PS7 and PS16 distributions (Fig. 1), the normalized mass of each blend is nonzero between the two peaks (i.e., around $M \approx 10^7$ g mol $^{-1}$) and the mass in this region increases with increasing c_{PS16} .

All of the test fluids (i.e., pure PS7 and PS16 solutions and their blends) are characterized in steady shear at 25 °C using an Anton-Paar MCR502 stress-controlled rotational rheometer fitted with a 50-mm-diameter 1° cone-and-plate geometry (see Fig. S1 [62]). As expected for dilute polymer solutions, the fluids have viscosities η close to that of the solvent $\eta_s \approx 57$ mPa s (the minimum solvent-to-total

viscosity ratio is $\eta_s/\eta \approx 0.8$), and the fluids exhibit weak to negligible shear thinning.

B. Capillary thinning experiments

When a liquid bridge confined between two interfaces becomes unstable to capillary forces (e.g., due to the separation between interfaces being increased), surface tension acts to break the bridge and form two separate droplets (one on each confining interface) in order to minimize the total surface area of the fluid. Neglecting inertia (which is demonstrated reasonable in the present experiments), during the VC thinning prior to breakup of a viscous Newtonian fluid, the liquid bridge develops an hourglass shape with a minimum diameter D at the midpoint (or neck) that reduces linearly in time t [15,16]. The radial squeezing at the neck generates an axial extensional flow with a strain rate $\dot{\epsilon}$ that increases with inverse proportionality to D as $\dot{\epsilon} = (-2/D)dD/dt$ [16,18], until the singular point of pinch-off where the fluid neck breaks and two separate droplets are formed. If polymer is added to the Newtonian fluid, the initial (inertialess) thinning behavior at early times is typically VC-like. However, as the extension rate in the fluid neck exceeds a critical value $\dot{\epsilon}_c \approx 0.5/\lambda$, coiled-up polymer molecules unravel and stretch [63–65], leading to the generation of an entropic elastic stress that resists the capillary pressure and retards the thinning process. When a sufficient quantity of polymer has stretched such that the elastic stress exceeds the viscous stress, the VC balance is superseded by the EC balance [17–19]. Now, when pinch-off would be expected for the Newtonian fluid, for the polymer solution the droplets that are formed on the two confining interfaces remain connected by a slender columnar filament. The diameter of the elastic filament is typically found to decay exponentially in time as $D \sim \exp[-t/(3\tau_{\text{EC}})]$, where according with the prediction of the Oldroyd-B model $\tau_{\text{EC}} \equiv \lambda$ [17,18,36,66]. Importantly, due to the exponential thinning in the EC regime, the extension rate in the filament becomes constant, with a value $\dot{\epsilon}_{\text{EC}} = 2/(3\tau_{\text{EC}})$ that is

self-selected by the fluid via the stress balance [17,18,36]. Several methods are utilized to generate and measure thinning capillary bridges for the purpose of finding τ_{EC} (and, indeed, other extensional rheological properties of complex fluids) [18,20–25,27,31,67], with the most widely known and used being the capillary-breakup extensional rheometer (CaBER) [18].

In this work, the capillary thinning response of each test fluid is measured at 25 °C using the low-inertia slow retraction method (SRM [20]) implemented on a commercial CaBER device (Haake CaBER 1, ThermoScientific). The test fluid is loaded such that it fills the approximately 1 mm gap between the flat horizontal surfaces of two coaxial circular plates of diameter 6 mm. The lower plate, which is mounted on a microadjustable stage, is slowly displaced downward, increasing the plate separation and causing the fluid to neck and form a capillary bridge. When the gap between the plates has become sufficiently large, the liquid bridge becomes unstable and begins to self-thin toward eventual pinch-off. The entire filament thinning and breakup process is captured at high speed (either 1000 or 3000 frames per second, depending on the total time until pinch-off) using a Phantom Miro M310 high speed video camera (Vision Research). A high-intensity LED backlight (Fiber-Light, Dolan-Jenner) fitted with a telecentric lens (Edmund Optics) is used to render the image of the thinning liquid bridge in sharp silhouette. The high-speed camera is fitted with a $6.5\times$ zoom lens (Edmund Optics) providing a

resolution on the fluid filament of approximately 5 μm per pixel, which is calibrated from an image of a 1-mm-diameter wire. A MATLAB program is used to process the resulting high-frequency image sequences first by thresholding and then using edge detection to extract $D(t)$ at the midpoint between the two confining plates. The value of τ_{EC} is extracted in the exponentially decaying region of $D(t)$, as per the Oldroyd-B model. Measurements on each fluid are repeated five times with freshly loaded samples and with excellent reproducibility. Because of recent reports that the measurement of τ_{EC} by the SRM method can depend on the plate diameter [31,33], we also test several fluids with plates of 4 and 8 mm diameter provided as standard with the commercial CaBER system. We found no systematic variation of the EC thinning dynamics over this range of plate size (see Fig. S2 [62]).

III. RESULTS

A. Qualitative imaging of capillary thinning

To highlight the fundamental phenomenon of interest that we report in this paper and which we believe can explain the concentration dependence of τ_{EC} , in Fig. 3 we present several exemplary time series of images depicting the capillary thinning of selected PS solutions. Here, the thinning of a 500 ppm solution of PS7 with no added PS16 [Fig. 3(a)] appears to be minimally affected by the addition of 5 ppm of PS16 [Fig. 3(b)]. By contrast, the addition of

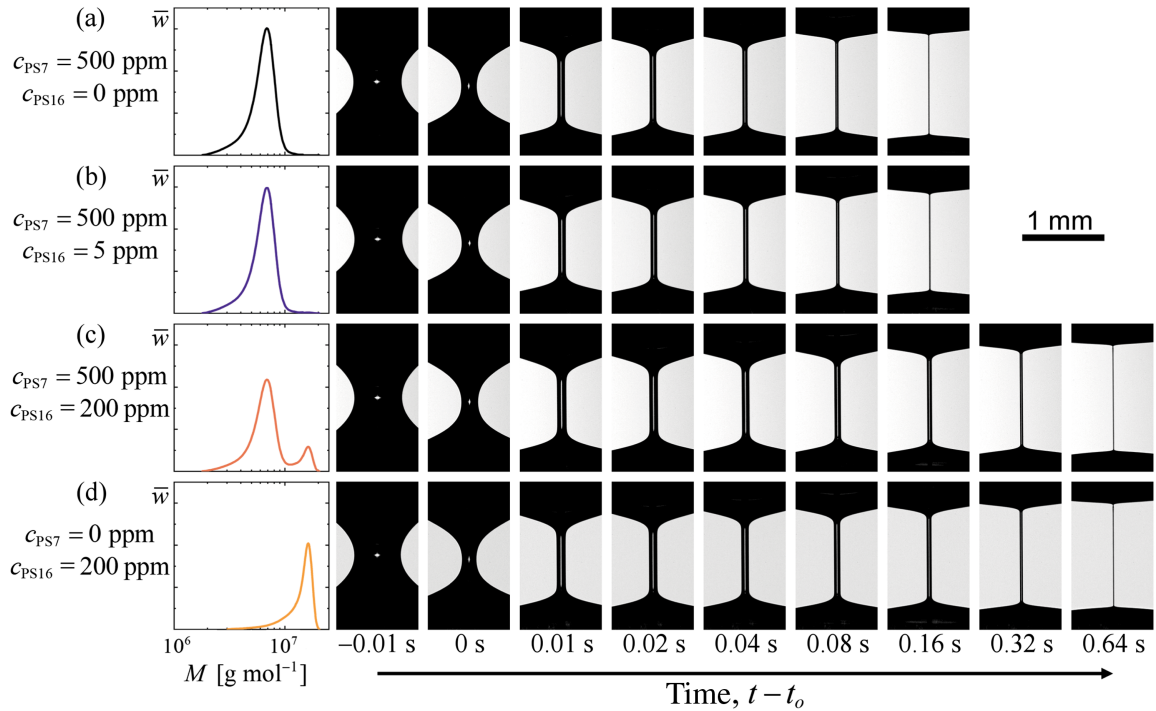


FIG. 3. Imaging of the capillary thinning of a few exemplary polymer solutions characterized by the MWDs shown to the left: (a) 500 ppm of PS7 in pure solvent, (b) 500 ppm of PS7 plus 5 ppm of PS16, (c) 500 ppm of PS7 plus 200 ppm of PS16, and (d) 200 ppm of PS16 in pure solvent. The time is indicated below the images where t_o is the time at the onset of elastocapillarity.

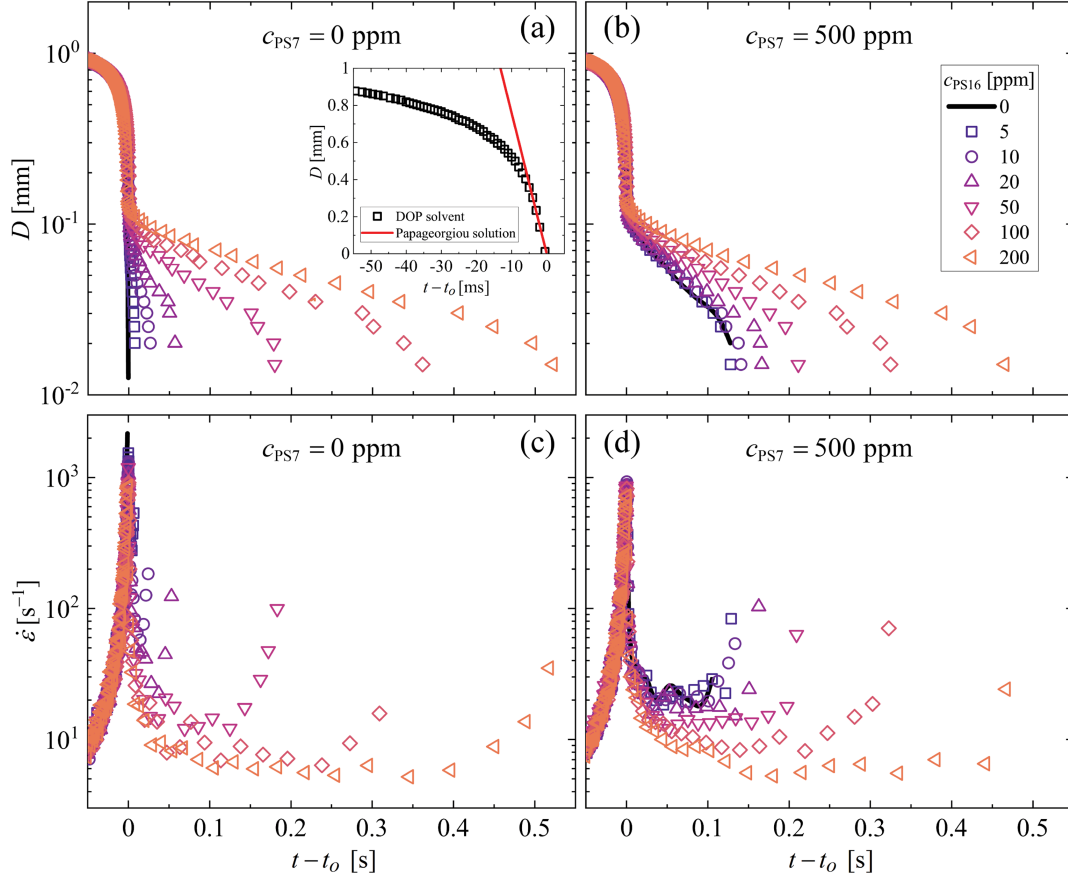


FIG. 4. Comparison between the capillary thinning response of solutions of PS16 in pure solvent ($c_{PS7} = 0$ ppm) and mixtures of PS16 with 500 ppm of PS7. (a), (b) Filament diameter as a function of time for $c_{PS7} = 0$ ppm and $c_{PS7} = 500$ ppm, respectively. (c), (d) Extension rate as a function of time for $c_{PS7} = 0$ ppm and $c_{PS7} = 500$ ppm, respectively. The inset in (a) shows the thinning of the pure Newtonian solvent (DOP), which close to pinch-off collapses onto the Papageorgiou similarity solution, indicating VC thinning dynamics.

200 ppm of PS16 to a 500 ppm solution of PS7 [Fig. 3(c)] results in a significantly [approximately $\mathcal{O}(4\times)$] longer time until pinch-off, and the thinning dynamics appear similar to those of a solution of pure 200 ppm PS16 with no PS7 in the mixture [Fig. 3(d)].

Qualitatively, it appears from the results shown in Fig. 3 that if c_{PS16} is low, then the PS7 component dominates the capillary thinning response. However, if c_{PS16} is high enough, then the PS16 component dominates the behavior. We therefore question the critical concentration conditions for the PS16 to dominate the dynamics, the understanding of which we anticipate should lead toward some fundamental insight into how polymer molecular weight and concentration mutually influence elastocapillary filament thinning.

B. Capillary thinning dynamics

Important details on how the capillary thinning dynamics depend on the fluid composition can be elucidated by plotting filament diameter versus time curves such as those

shown in Figs. 4(a) and 4(b). Note that in these plots the time axis is shifted by the value t_o marking the onset of the EC thinning regime for the polymer solutions or the breakup time for the pure solvent. Time t_o for the polymer solutions occurs at the peak in the respective extension rate versus time plot [see Figs. 4(c) and 4(d)]. In Fig. 4(a), we present filament thinning profiles for pure PS16 solutions (i.e., $c_{PS7} = 0$ ppm) over the full range of c_{PS16} . At short times $t < t_o$, the data for the PS16 solutions lie on top of those for the pure DOP solvent (i.e., $c_{PS16} = 0$ ppm, solid black line). For the solvent, $D \rightarrow 0$ at $t = t_o$ (i.e., pinch-off occurs). However, the thinning curves for the polymer solutions deviate from Newtonian-like behavior at time $t = t_o$ and enter the exponential EC thinning regime for $t > t_o$. At $c_{PS16} = 5$ ppm, the breakup time is very short [$t - t_o \sim \mathcal{O}(\text{ms})$] and the thinning in the EC regime ($t > t_o$) is relatively fast. With increasing c_{PS16} , the thinning rate in the EC regime progressively decreases and the time to pinch-off progressively increases. When the same concentrations of PS16 are blended with 500 ppm of PS7, the thinning curves are markedly shifted, at least for low values

of c_{PS16} . For $c_{\text{PS16}} \leq 10$ ppm, the EC thinning in combination with 500 ppm of PS7 [Fig. 4(b)] is significantly slower than it is in the presence of 0 ppm of PS7 [Fig. 4(a)]. At these low concentrations, the presence of PS16 appears to have little effect on the thinning dynamics compared to the background 500 ppm PS7 solution [shown by the solid black line in Fig. 4(b)]. However, at higher concentrations of $c_{\text{PS16}} \geq 20$ ppm, there is a noticeable reduction in the thinning rate and increase in the time to pinch-off. For $c_{\text{PS16}} \geq 100$ ppm, a comparison between the thinning profiles shown in Figs. 4(a) and 4(b) reveals that the response is largely unaffected by the presence (or not) of PS7 in the blend.

The plots of extension rate versus time provided in Figs. 4(c) and 4(d) show how $\dot{\epsilon}$ increases monotonically during the Newtonian-like (or VC) thinning regime ($t < t_o$), reaching a peak at t_o . The time t_o marks the instant at which the elastic stress due to the stretching of dissolved polymer begins to exceed the viscous stress due to the solvent, i.e., the onset of the EC thinning regime. Subsequently, for $t - t_o > 0$, the extension rate decreases to the plateau value $\dot{\epsilon}_{\text{EC}} = 2/(3\tau_{\text{EC}})$. It is worthwhile noting that the value of $\dot{\epsilon}_{\text{EC}}$ progressively decreases for increasing c_{PS16} for both cases of $c_{\text{PS7}} = 0$ ppm [Fig. 4(c)] and $c_{\text{PS7}} = 500$ ppm [Fig. 4(d)].

Note that the inset in Fig. 4(a) shows that, close to pinch-off, the thinning data for the Newtonian DOP solvent collapse onto the similarity solution derived by Papageorgiou [15,16], given by $D/2 = 0.0709(\gamma/\eta_s) \times (t_o - t)$. This confirms that the thinning at early times $t < t_o$ is controlled by the VC stress balance. This is also consistent with an estimate of the Ohnesorge number $\text{Oh} = \eta_s/\sqrt{\rho\gamma(D/2)}$, which compares timescales for viscosity-controlled and inertia-controlled breakup [68]. Taking a value of $D \approx 1$ mm from the onset of self-thinning, we estimate $\text{Oh} \approx 0.46$, greater than the threshold value $\text{Oh}_c = 0.2077$, above which breakup is dominated by viscous effects [20].

C. Characteristic EC thinning times

Characteristic times τ_{EC} extracted in the EC regime for all of the tested polymer solutions are displayed in Fig. 5, where Figs. 5(a) and 5(b) report the same data but presented on linear-linear and log-log axes, respectively. In these plots, the solid horizontal lines mark the values of τ_{EC} determined for pure PS7 solution (i.e., with $c_{\text{PS16}} = 0$ ppm), and solid black data points connected by solid lines mark the values of τ_{EC} determined for pure PS16 solutions (i.e., with $c_{\text{PS7}} = 0$ ppm). The open colored data points connected by dashed lines mark τ_{EC} for blends of PS7 and PS16, with c_{PS7} indicated in the legend and c_{PS16} indicated on the horizontal axis. Shaded regions about the data points and/or lines indicate the standard deviation over five repeated measurements of τ_{EC} .

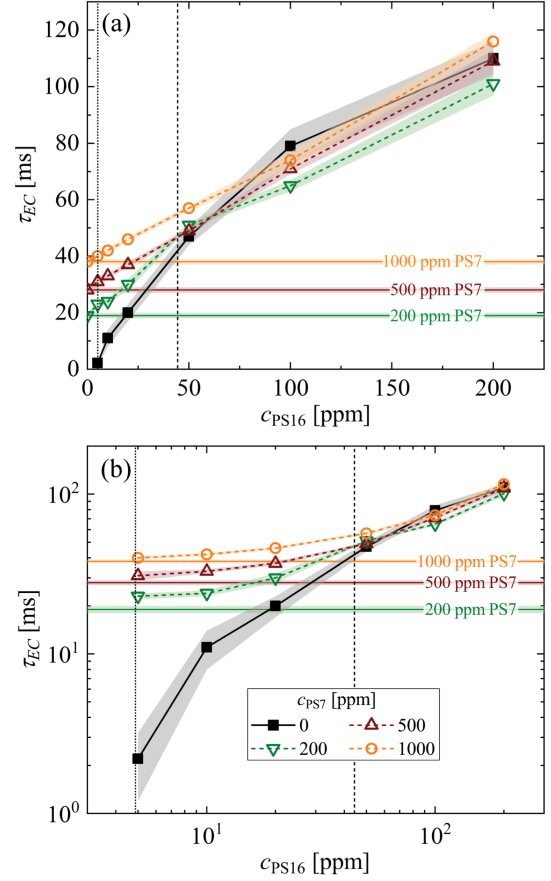


FIG. 5. Values of τ_{EC} determined for all tested polymer solutions as a function of the PS16 concentration. Thin horizontal solid lines indicate τ_{EC} for the respective PS7 concentration and $c_{\text{PS16}} = 0$ ppm. Shaded regions about the data indicate one standard deviation over five repeated measurements. The vertical dotted line marks the value of $c_{\text{min,PS16}} = 4.8$ ppm, and the vertical dashed line marks the value of $c_{\text{low,PS16}} = 44$ ppm. (a) and (b) show the same data but on linear-linear and log-log scales, respectively.

For pure solutions of PS16, τ_{EC} increases monotonically with increasing c_{PS16} . For $c_{\text{PS16}} = 5$ ppm (which is only slightly above $c_{\text{min,PS16}} = 4.8$ ppm, marked by the vertical dotted line), τ_{EC} is difficult to measure at only approximately 2 ms and it appears would become immeasurable at lower concentrations. However, we note that the apparent agreement between our measurement limit and $c_{\text{min,PS16}}$ [Eq. (3)] is probably coincidental, since $c_{\text{min,PS16}}$ is estimated for M_p and in no way accounts for the MWD.

For the polymer solution blends with low $c_{\text{PS16}} \lesssim 10$ ppm, the measured value for τ_{EC} is close to, but slightly greater than, that measured for $c_{\text{PS16}} = 0$ ppm (i.e., for the respective pure PS7 solution). However, with increasing $c_{\text{PS16}} \gtrsim 50$ ppm, τ_{EC} for all of the blends (regardless of PS7 concentration) tends closely to that of the pure PS16 solution (i.e., with $c_{\text{PS7}} = 0$ ppm). The concentration

above which the PS16 appears to dominate the thinning dynamics closely aligns with the value of $c_{\text{low,PS16}} = 44$ ppm (marked by the vertical dashed line). However, as also noted for c_{min} , c_{low} is computed based on the peak molecular weight M_p and does not account for the MWD. The agreement is likely coincidental and due to the very low-PDI of the PS16 polymer sample. We return to this point later in our discussion.

Notice in Fig. 5 that, although our data are quite coarsely spaced in concentration, we see no tendency toward a constant value of τ_{EC} for values of c_{PS16} below the stretched overlap concentration $c_s^* \approx 20$ ppm [Eq. (5) and Table I] defining the supposed upper limit of ultra-dilution [42]. Campo-Deaño and Clasen argue that for $c_{\text{min}} < c < c_{\text{low}}$ a measurement of τ_{EC} will be spurious due to the imminent onset of finite extensibility effects subsequent to t_o [19,20]. It is clear from Table I that (for our test fluids) $c_{\text{min}} < c_s^* < c_{\text{low}}$, perhaps explaining why we see no concentration independent plateau in τ_{EC} for low c_{PS16} .

D. Interpretation of the results

We interpret the data summarized in Figs. 4 and 5 as described in the following. We know with confidence that (i) the relaxation time of the polymer depends on molecular weight as $\lambda \sim M^{3/2}$ [69,70], (ii) polymer stretching in the flow is predicted for $\dot{\epsilon}_c \sim 1/\lambda$ [63,64,71], and (iii) in the VC regime the extension rate $\dot{\epsilon}$ increases with time [as shown by Figs. 4(c) and 4(d) for $t < t_o$]. Therefore, we expect that, as time proceeds during the VC regime and $\dot{\epsilon}$ increases, progressively shorter, lower- M molecules in the MWD will begin to stretch. We assume that eventually, at time $t = t_o$, a sufficient fraction of the MWD will have become stretched such that the total accumulated elastic stress exceeds the viscous stress, therefore resulting in the onset of the EC regime.

This concept is outlined in Fig. 6, where we schematically represent an idealized extension rate versus time curve for a thinning polymer solution overlaid on a distribution of critical strain rates $\dot{\epsilon}_c(M) \sim 1/M^{3/2}$ corresponding to a hypothetical MWD. Figure 6 illustrates that (in principle) the peak extension rate $\dot{\epsilon}_o$ achieved at time t_o corresponds to the critical extension rate $\dot{\epsilon}_{c,o}$ of the shortest polymers to stretch (with molecular weight M_o) prior to the onset of the EC regime. All polymers with $M > M_o$ (thus, $\dot{\epsilon}_c < \dot{\epsilon}_{c,o}$, shaded region) are assumed to have already stretched at earlier times $t < t_o$. The total polymer concentration illustrated in Fig. 6 is arbitrary. For increasing (decreasing) polymer concentrations, t_o is expected to shift left (right), since less (more) of the MWD is required to stretch in order to generate sufficient elastic stress for an EC regime to manifest. Correspondingly, $\dot{\epsilon}_o$ is expected to decrease (increase) in order to match $\dot{\epsilon}_{c,o}$. The expected variation of $\dot{\epsilon}_o$ with polymer concentration is observed experimentally [e.g., Figs. 4(c) and S3 [62]] and was also reported in

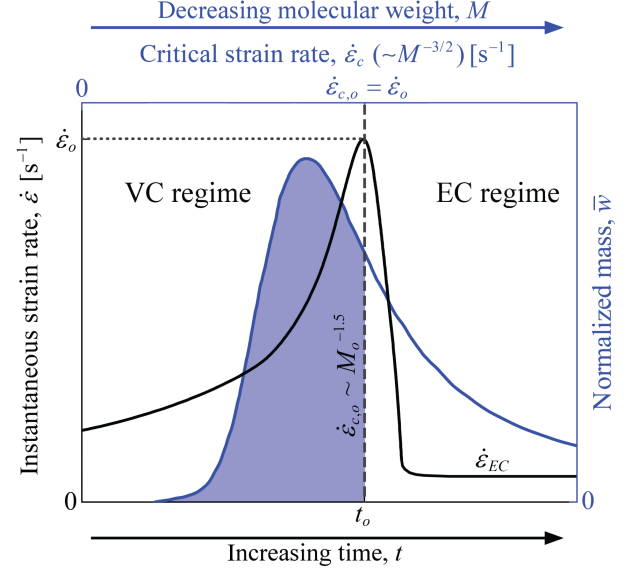


FIG. 6. Sketch outline of the proposed hypothesis involving the stretching of a portion of the MWD distribution during the VC thinning regime. The solid black line represents an idealized extension rate versus time curve in a self-thinning capillary neck. The solid blue line represents a distribution of critical extension rates $\dot{\epsilon}_c$ for the stretching of the polymers in a hypothetical MWD. The horizontal dotted line marks the peak extension rate $\dot{\epsilon}_o$ at time $t = t_o$ marking the VC-EC transition. The vertical dashed line marks time t_o and also the critical extension rate $\dot{\epsilon}_{c,o} (\equiv \dot{\epsilon}_o)$ of the shortest polymers to stretch (with $M = M_o$) before the onset of the EC regime. The shaded region under the blue curve indicates the portion of the MWD with $M > M_o$ that should have already stretched (or started to stretch) prior to t_o .

Ref. [27]. However, we find considerable uncertainty in the extraction of $\dot{\epsilon}_o$, since it is represented by a single data point computed by differentiation of noisy raw data.

Returning to the experimental results in Figs. 4 and 5, we suggest that, for the pure PS16 solutions, if $c_{\text{PS16}} \lesssim 5$ ppm, then the whole of the MWD can stretch without generating enough elastic stress to induce an EC regime. If c_{PS16} is small but $\gtrsim 5$ ppm, then we suggest that most of the PS16 MWD must stretch prior to the onset of the EC regime; thus, the EC regime is controlled by a low- M portion of the MWD. As c_{PS16} is increased, a smaller fraction of the MWD is required to stretch before the elastic stress exceeds the viscous stress. Thus, the EC regime is achieved within a higher molecular weight portion of the distribution, the longer relaxation time of which results in a larger value for τ_{EC} .

In terms of the polymer blends, even the smallest concentration of PS16 contributes some elastic stress when deformed; thus, τ_{EC} measured for the blend is always greater than that measured for the respective pure PS7 solution. Recall that the tails of the PS7 and PS16 MWDs have an overlapping region (see Fig. 1). Accordingly, although a pure PS16 solution at $c_{\text{PS16}} = 5$ ppm can by itself induce an EC regime, it is still possible for part of the

high- M tail of the PS7 distribution to stretch and contribute to the total elastic stress. At higher values of PS16 (i.e., $c_{\text{PS16}} \gtrsim 50$ ppm), we suggest that sufficient elastic stress is derived from the high- M tail of the PS16 MWD (at molecular weights beyond the range of overlap) so that none of the PS7 MWD is required (or able) to deform. Accordingly, at these high PS16 concentrations, the PS7 plays essentially no role in the emerging filament thinning dynamics, and τ_{EC} for the blend closely matches that for the respective pure PS16 solution.

E. A simple model description

Our hypothetical explanation for our results suggests a relatively simple qualitative description. Closely following the procedure used in the derivation of the c_{min} criterion [Eq. (3)] [19], we aim to compute and sum the elastic stress contributions arising from the progressive stretching of decreasing molecular weight species in a distribution. We bin the normalized MWDs such as illustrated in Figs. 1 and 2 into “modes” i each spanning a range of $M = 20000 \text{ g mol}^{-1}$, where mode $i = 1$ has the highest M , mode $i = 2$ the second-highest M , etc. For a given total polymer concentration $c = c_{\text{PS7}} + c_{\text{PS16}}$, we use the normalized MWD to compute the concentration c_i of polymer contained in each mode. For each mode with molecular weight M_i , we compute (i) the polymer extensibility L_i [according to Eq. (1)], (ii) the Zimm relaxation time $\lambda_{Z,i}$ [according to Eq. (2)], and (iii) the elastic modulus $G_i = c_i N_A k_B T / M_i$ [19,72]. The elastic stress contributed by each mode when fully stretched is estimated as [19]:

$$\Delta\sigma_{p,i} = 2G_i\lambda_{Z,i}L_i^2\dot{\epsilon}. \quad (6)$$

Note that at a given strain rate it takes finite time for macromolecular strain to accumulate, and so it is unreasonable to expect every stretching mode to attain full extension within time $t \leq t_o$. However, Eq. (6) should provide an estimated upper bound for the stress contributed by each mode.

The viscous stress due to the solvent is given simply by $\Delta\sigma_s = 3\eta_s\dot{\epsilon}$, where the factor 3 represents the Trouton ratio in uniaxial extensional flow.

We sum the elastic stress contributions from progressively shorter modes, until the total exceeds the viscous stress, i.e.:

$$\frac{2}{3\eta_s} \sum_{i=1}^{i=o} G_i\lambda_{Z,i}L_i^2 > 1. \quad (7)$$

Finally, we extract the properties of the last (shortest) mode in the summation, specifically, M_o and $\lambda_{Z,o}$. This process is approximately predicting the stretched portion of the MWD with $M \geq M_o$ at the onset of the EC regime at $t = t_o$. We are not attempting to account for any relaxation

of shorter modes as the extension rate decreases toward the plateau value $\dot{\epsilon}_{\text{EC}}$ subsequent to t_o . Implicit assumptions here are that molecules are completely noninteracting and that all modes adopt the Zimm relaxation time regardless of the input total polymer concentration. We also point out that the Zimm relaxation times refers to the time for a coiled non-free-draining polymer molecule to diffuse through the solvent a distance equal to its own size and does not necessarily describe a timescale related with stretching and/or recoil of the chain [58]. Therefore, we do not necessarily expect to obtain a quantitative agreement between $\lambda_{Z,o}$ and our measured values for τ_{EC} . However, $\lambda_{Z,i}$ is conveniently calculable and does give the expected molecular weight scaling for stretching timescales of ideal polymers in extensional flows [69,70,73–75].

Figures 7(a)–7(e) illustrate the effect of varying the total polymer concentration c on the portion of the PS16 MWD that must stretch in order to induce an EC regime, where the stretched modes are indicated by shading under the MWD curve. Here, since $c_{\text{PS7}} = 0$ ppm, then $c \equiv c_{\text{PS16}}$. At very low $c_{\text{PS16}} = 3$ ppm [Fig. 7(a)], even when the whole MWD is fully stretched, there is insufficient elastic stress to overcome the viscous stress; hence, we predict no EC regime, and we cannot obtain values for M_o or $\lambda_{Z,o}$ in this case. The elastic stress contributed by the whole of the fully stretched PS16 MWD remains below the viscous stress as long as $c_{\text{PS16}} \lesssim 5.4$ ppm. We can define the concentration $c'_{\text{min,PS16}} \approx 5.4$ ppm as a measure of the c_{min} criterion [Eq. (3)] [19] that accounts for the entire PS16 MWD (though which in this case happens to be coincidentally close to the value $c_{\text{min,PS16}} = 4.8$ ppm estimated based on a single molecular weight M_p). For $c_{\text{PS16}} = 5.5$ ppm [$\gtrsim c'_{\text{min,PS16}}$, Fig. 7(b)], most of the PS16 distribution must stretch in order to generate the required elastic stress; hence, M_o is located in the low- M tail of the MWD with $\lambda_{Z,o} = 1.5$ ms. With increasing c_{PS16} through Figs. 7(c)–7(e), progressively less of the MWD is required to stretch in order for the viscous stress to be exceeded; thus, M_o shifts toward the high- M tail of the MWD, and $\lambda_{Z,o}$ progressively increases.

Figures 7(f)–7(j) illustrate the effect of varying c_{PS16} in a blend with $c_{\text{PS7}} = 50$ ppm (i.e., such that the total polymer concentration $c = c_{\text{PS16}} + 50$ ppm). At $c_{\text{PS16}} = 3$ ppm, whereas the pure PS16 solution [Fig. 7(a)] could not yield values for M_o or $\lambda_{Z,o}$, in the corresponding blend [Fig. 7(f)] the stretching of the high- M tail of the PS7 MWD leads to sufficient elastic stress to induce the EC regime at $M_o = 8.6 \times 10^6 \text{ g mol}^{-1}$ with $\lambda_{Z,o} = 1.4$ ms. As observed for pure PS16 solutions, increasing c_{PS16} in the blend (thus increasing c) causes M_o to shift to progressively higher values. At $c_{\text{PS16}} = 5.5$ ppm and $c_{\text{PS16}} = 6$ ppm, M_o for the pure PS16 solution occurs within the range where the PS7 and PS16 MWDs overlap [see Figs. 1, 7(b), and 7(c)]. Thus, at these values of c_{PS16} in the blend [see Figs. 7(g) and 7(h)], M_o is greater (and $\lambda_{Z,o}$ longer) than that of the pure PS16 solution due to the increased concentration of

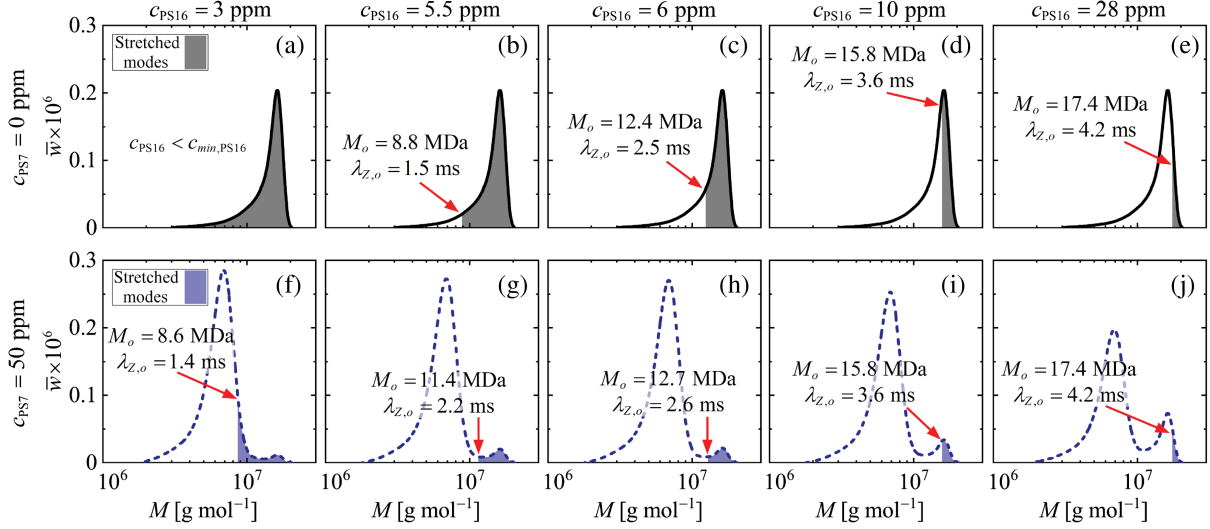


FIG. 7. Values of the Zimm relaxation time $\lambda_{Z,o}$ corresponding to the lowest molecular weight mode M_o at which the accumulated elastic stress exceeds the viscous stress, computed by summation of the elastic stress contributions of each fully stretched mode [see Eq. (7) and text description]. Shaded regions underneath the curves indicate the portion of the MWD that must become fully stretched during the VC thinning regime in order to induce a VC-EC transition. (a)–(e) are obtained for MWDs with $c_{PS7} = 0$ ppm and (f)–(j) for $c_{PS7} = 50$ ppm, with corresponding values for c_{PS16} indicated at the top of the figure.

polymer c_i in the overlapping modes. As c_{PS16} is further increased to 10 ppm and above, M_o for the pure PS16 solution shifts beyond the range of overlap between the two MWDs. In these cases, M_o for the blend [Figs. 7(i) and 7(j)] becomes identical to that of the pure PS16 [Figs. 7(d) and 7(e)]; i.e., sufficient elastic stress is developed by the high- M portion of the PS16 MWD such that, in the blend, none of the PS7 MWD is required to stretch. In a real capillary thinning experiment, this situation would correspond to a case in which the extension rate prior to the EC regime never became high enough to stretch any of the molecules in the PS7 MWD.

Note that here we have used a blend with lower c_{PS7} than used experimentally simply to permit a slightly clearer visualization of the small amount of PS16 in the blend. However, precisely the same principles apply for blends with higher PS7 concentrations.

In Fig. 8(a), we present computed values of $\lambda_{Z,o}$ as a function of c_{PS16} for various blends at different values of c_{PS7} , mimicking the presentation of the experimental data in Fig. 5(a). Calculations are performed at sufficiently small increments in c_{PS16} to generate effectively continuous line plots. The simple summation of elastic stresses performed to obtain M_o and $\lambda_{Z,o}$ [Eq. (7)] helps to corroborate the

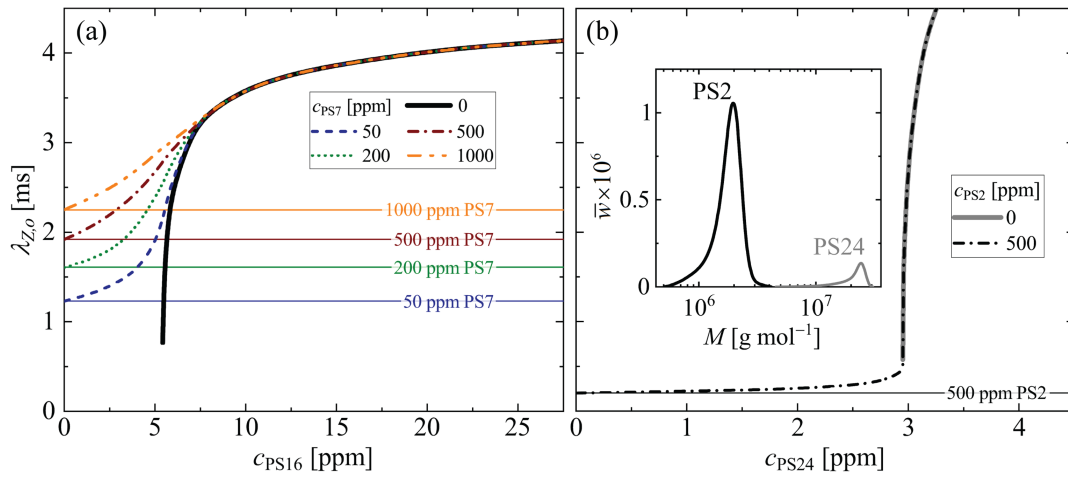


FIG. 8. Values of the Zimm relaxation time of the last fully stretched mode $\lambda_{Z,o}$ at the point where the elastic stress exceeds the viscous stress, computed according to Eq. (7). (a) Data determined using the overlapping MWDs for PS7 and PS16 (see Fig. 1) with various values of c_{PS7} and for refined increments in c_{PS16} ; (b) data determined using the synthetic nonoverlapping MWDs for PS2 and PS24 (as shown in the inset), with $c_{PS2} = 500$ ppm and for refined increments in c_{PS24} .

hypothesis derived on the basis of our experiments. In Fig. 8(a), our calculations show that, for pure PS16 solutions, for $c > c'_{\min, \text{PS16}} \approx 5.4$ ppm the relaxation time increases abruptly and monotonically. Relaxation times of the PS7 and PS16 blends are close to (but always greater than) that of the pure PS7 solution for low $c_{\text{PS16}} < c'_{\min, \text{PS16}}$, since even at vanishing concentrations stretching of the PS16 contributes finite elastic stress. With increasing $c_{\text{PS16}} < c'_{\min, \text{PS16}}$, the relaxation time of the blend diverges from that of the respective pure PS7 solution due to the progressively increasing elastic stress contributed by stretched modes in the PS16 MWD. At intermediate PS16 concentrations $c'_{\min, \text{PS16}} < c_{\text{PS16}} \lesssim 8$ ppm, even though the PS16 MWD alone can generate sufficient elastic stress to provide a value for $\lambda_{Z,o}$, the relaxation times for the blends remain greater than for the pure PS16. This is due to the overlap between the PS7 and PS16 MWDs and the increased concentration of material in the shared modes. At higher values of $c_{\text{PS16}} \gtrsim 8$ ppm, the relaxation time of each blend matches that of the pure PS16, since sufficient stress is generated by the stretching of the highest- M modes in the PS16 MWD that none of the modes within the PS7 MWD are required to stretch. The shorter timescales yielded by our model relative to the experiment may be explained by (i) our use of the Zimm time estimate in the model and (ii) the likelihood that shorter stretched modes relax subsequent to t_o while some longer modes may be continuing to stretch, neither of which are accounted for. The lower PS16 concentrations in the model results are possibly explained because we are estimating an upper bound for the elastic stress by assuming each stretching mode reaches full extension. Given the significant simplifying assumptions underlying our retrieval of $\lambda_{Z,o}$ by Eq. (7), the clear qualitative agreement between Figs. 5(a) and 8(a) is remarkable and compelling, with all the essential trends of the experimental data being captured by our simple model. A better quantitative agreement with the experiment would likely be obtained by full multimodal FENE simulations, beyond the scope of the current work.

The overlap between the PS7 and PS16 MWDs complicates our analysis somewhat, but we are also able to use our model to examine the response of blends whose MWDs do not overlap at the extremes. Unfortunately, this is complicated experimentally due to the very long tails of real MWDs and because the short relaxation times of low- M polymers are hard to measure reliably. For these reasons, obtaining two polymer samples, both with measurable τ_{EC} at dilute concentrations, and with sufficiently widely separated values of M_p is challenging. In the case of applying our simple model to the problem, noninteracting MWDs are easily generated by shifting the PS7 MWD by a factor 1/3.5 and by shifting the PS16 MWD by a factor 1.5 along the M axis, thus providing synthetic “PS2” and “PS24” MWDs, as illustrated in the inset in Fig. 8(b). The

main plot in Fig. 8(b) shows values of $\lambda_{Z,o}$ computed for pure PS24 solutions, and for blends of 500 ppm PS2 with PS24, over a range of c_{PS24} . For the pure PS24 solutions, we cannot determine a value for $\lambda_{Z,o}$ if $c_{\text{PS24}} \lesssim 3$ ppm, since below this concentration the elastic stress is below the viscous stress even if the whole of the PS24 MWD is fully stretched. Hence, we can define $c'_{\min, \text{PS24}} \approx 3$ ppm. For increasing concentrations of $c_{\text{PS24}} > 3$ ppm, $\lambda_{Z,o}$ for the pure PS24 solutions increases abruptly. For the blends with 500 ppm PS2 and $0 < c_{\text{PS24}} \lesssim 3$ ppm, $\lambda_{Z,o}$ can be determined and is close to that of the pure 500 ppm PS2 solution. In this range of PS24 concentration, $\lambda_{Z,o}$ increases slightly with increasing c_{PS24} due to the small, but increasing, elastic stress contribution arising from the full stretching of the entire PS24 MWD, which shifts M_o progressively toward the high- M tail of the PS2 MWD. Since there is now no cross-coupling between extreme modes in the two MWDs, for $c_{\text{PS24}} \gtrsim 3$ ppm the PS24 dominates the response of the blend, with the PS2 MWD contributing precisely zero elastic stress in our simple model. Thus, for $c_{\text{PS24}} \gtrsim 3$ ppm, $\lambda_{Z,o}$ for the blend precisely matches that for the pure PS24 solution.

IV. DISCUSSION

With our aim being to obtain new insight into the importance of the molecular weight distribution of real polymer samples on EC thinning measurements with dilute polymer solutions, we have performed experiments with blends of ideal and well-characterized polymer samples having distinct peak molecular weights M_p and narrow MWDs. By fixing the concentration of the lower- M_p component to be relatively high and by varying the concentration of the higher- M_p component in the blend, we have demonstrated that the component which dominates the EC thinning dynamics can be switched. The results suggest that, for any given MWD with $\text{PDI} > 1$, the dominant mode (or modes) controlling the EC thinning of polymer solutions will depend on the total concentration of polymer c in the solution.

The transition into the EC thinning regime depends on the elastic stress dominating over the viscous stress in the self-thinning capillary bridge. The elastic stress that drives this transition is generated by the stretching of polymer during the initial VC thinning regime in which the strain rate increases monotonically with time. We, therefore, hypothesize that over time progressively shorter polymers in the MWD begin to stretch and contribute to the elastic stress. Depending on the total polymer concentration, a different fraction of the MWD will be required to stretch (or to start to stretch) in order to overcome the viscous stress and induce the onset of EC thinning. Therefore, the EC thinning dynamics depend on c , since for increasing c a higher molecular weight of polymer with a longer relaxation time is effectively controlling the EC thinning process.

Our findings highlight how the differential contributions of molecular weight fractions contribute to and influence the elastocapillary thinning process. While we do not directly observe individual polymer chain dynamics, our results reflect an ensemble manifestation of molecular individualism [71,76,77], where the accumulation of elastic stress contributions due to the progressive stretching of decreasing molecular weights within the distribution dictate the elastocapillary thinning dynamics by feeding back on the flow and setting the self-selected extension rate.

Based on the assumption of sequential polymer stretching within the VC regime, we are able to qualitatively capture our experimental results through a simplified model in which we sum the elastic stress contributions of progressively decreasing modes in the MWD until the accumulated elastic stress exceeds the viscous stress (i.e., until the elastic stress passes the threshold for onset of the EC regime in a capillary thinning experiment). Given the simplicity of the model and the implicit assumptions therein, we consider the qualitative agreement that it yields with the experiment amounts to compelling support for our hypothesis. This shows that the measured value of τ_{EC} can depend on the concentration of polymer in solution even in the absence of interpolymer interactions, simply due to the spread of timescales present in the molecular weight distribution. This observation means that defining concentration criteria for ultradiluteness such as c_s^* [Eq. (5) [42]] may not be necessary in order to understand the concentration dependence of τ_{EC} in dilute conditions. Instead, at least some degree of concentration dependence should simply be expected in the capillary thinning of polydisperse polymer systems.

Regarding other concentration criteria, for the PS16 sample used here, c_{min} and c_{low} appear to be reasonable indicators of the fluid response to capillary thinning (see Fig. 5). This is almost certainly because of the very low PDI of the polymer sample; it can easily be conceived of two homologous polymer samples with different PDI but equal M_p that would have the same values for c_{min} and c_{low} but would be expected to display contrasting filament thinning dynamics at equal given concentration due to the different MWD [49]. We have shown that the c_{min} criterion [Eq. (3) [19]] can be adapted to account for polydispersity (if the MWD is known *a priori*) and takes meaning as the concentration below which an EC regime would not be observed even if the whole of the MWD became fully stretched. However, for polydisperse systems, the c_{low} criterion [Eq. (4) [20]] appears to lose significance. This criterion defines the concentration of polymer required to induce an EC regime during the earlier stages of stretching, a requirement for the extraction of the “true” relaxation time from the exponential decay constant. However, c_{low} implicitly assumes the system of interest is monodisperse and that all of the polymers in the solution will deform at the same extension rate. Considering the c_{low} criterion in

context of a MWD, a question arises about which of the many disperse polymers present needs to be stretching in order to induce the EC regime (essentially the question that we ask in this paper). We see no straightforward way to estimate c_{low} for a polydisperse system. Not only would the MWD need to be known *a priori*, but most likely a complex multimodal FENE analysis would be required. Campo-Deaño and Clasen suggest that, for polymer solutions at concentrations $c_{min} < c < c_{low}$, the extraction of τ_{EC} from a capillary thinning measurement yields a spurious estimate of the true polymeric relaxation time [19,20]. In contrast, our current results indicate that for any dilute polymer solution yielding an exponential thinning regime it may, in fact, be reasonable to extract a value for τ_{EC} and that the value retrieved should be related to some relaxation timescale of the fluid. Confoundingly, though, the extracted timescale will correspond to a concentration-dependent and, in general, unknown, molecular weight fraction of the MWD.

The current work (and also another recent work involving capillary thinning of solutions of polymers with various flexibilities [32]) reveals the great importance of the initial VC thinning stage prior to the onset of the EC regime. Previous work has shown that significant prealignment of stiffer polymeric systems can occur during the VC regime, while the present work shows that significant prestretching of more flexible polymers is also possible prior to the onset of elastocapillarity (as also suggested by another recent study [33]). This prestretching and prealignment determine what remains to be stretched and/or aligned during the EC regime itself and, therefore, dictate exactly what component of the fluid the extracted value of τ_{EC} corresponds to.

As discussed in Ref. [32], elastocapillary thinning measurements can provide useful timescales relevant to the observation of nonlinear elastic effects in extensional flows of complex fluids. However, our current results have clear implications for extensional rheometry techniques based on capillary thinning measurements and may provide new understanding relevant to the interpretation of some previous results reported in the literature. For instance, the derivation of scaling laws for polymer relaxation times with concentration based on capillary thinning measurements made with highly disperse commercial polymers (e.g., Refs. [27,29,42]) is called into question, since it is clearly inadequate to relate such measurements to a single molecular weight defined by M_w or M_p . Any “concentration dependence” may not be solely due to concentration but may be significantly affected by the broad MWD. Apart from the concentration dependence of τ_{EC} , it also becomes clear why capillary thinning of very dilute polymer solutions can yield timescales shorter than expected based on estimates made for M_w or M_p (e.g., Refs. [19,29,42]). More fundamentally, issues related to the fluid’s self-selection of the strain rate in the EC thinning regime are brought into sharp clarity. Generally, in rheometry it is

desirable to impose the deformation rate and to be able to vary that imposed rate while measuring the steady state stress required to maintain it, an approach that allows a range of fluid timescales to be probed by the rheometrist. For a given polymer sample in the dilute regime, imposition of a controlled deformation rate should result in the same fraction of the MWD of the sample being deformed regardless of concentration. This is obviously not possible in a capillary thinning experiment, which is self-evident since the deformation rate in the EC regime depends on concentration; see Figs. 4(c) and 4(d). In most branches of rheometry, it would be implicitly understood that, for the application of different strain rates, different fluid timescales are being probed in the experiment. At a most basic level, here we are proposing that exactly the same concept applies in the case of capillary thinning-based extensional rheometry techniques.

V. CONCLUSIONS

The thinning of fluid filaments under the action of capillary pressure impacts widespread important processes and is utilized for the measurement of characteristic “relaxation times” of complex fluids such as polymer solutions. An important question is why the determination of such characteristic times depends on the polymer concentration even when the fluid is dilute. This is usually explained by invoking intermolecular interactions occurring in fluids that are not “ultradilute” and by “self-concentration” effects as the polymer stretches [19,39,42]. Although relaxation times are undoubtedly affected by interpolymer interactions above some concentration limit (normally considered as being $c > c^*$), our experiments and simple calculations indicate that the polymer molecular weight distribution also requires accounting for and may even fully explain the concentration dependence of elastocapillary timescales observed at concentrations $c < c^*$.

Our results show how a concentration-dependent portion of a polymer’s molecular weight distribution can become stretched during the Newtonian-like thinning stage occurring prior to the onset of elastocapillarity. This then determines which polymers in the distribution will control the rate of thinning during the subsequent elastocapillary stage: For higher polymer concentrations, onset of elastocapillarity occurs at higher molecular weights. Alternatively, by considering the concentration-dependent extension rate achieved during elastocapillary thinning, it becomes self-evident that longer fluid timescales (hence, higher molecular weights) are being probed by the experiment as the polymer concentration is increased. The observed concentration dependence of elastocapillary timescales is, thus, a direct consequence of the inability to control the extension rate during capillary-driven self-thinning. This has significant implications for the application of capillary thinning to the acquisition of rheometric data and for the interpretation of data thus obtained.

Finally, we reiterate that, although we focus our discussion here on the relevance to extensional rheometry, an improved understanding of the important role of the molecular weight distribution could potentially benefit numerous practical applications that involve the capillary-driven thinning of viscoelastic fluids. We hope that this work should motivate future experimental, numerical, and theoretical studies aimed toward this goal.

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