Perspective

When Polymer Chains Are Highly Aligned: A Perspective on Extensional Rheology

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ABSTRACT: We provide a Perspective on recent findings in extensional rheology for polymer melts and solutions with different macromolecular architectures. For linear polymer systems, we focus on the argument of flow-induced friction reduction and provide our comments from an experimental point of view. For branched polymers, we provide our understanding on how to control extensional viscosity for polymers with different zero-shear-rate viscosity based on recent experimental results of star and comb polymer melts. For ring polymers, we summarize the recent progress in extensional rheology and provide our view on what would be interesting for further investigation. On the basis of the above results and discussions, we show that extensional rheology is complicated for even very simple molecular architectures. More data from both experiments and simulations are important for improvement of a fundamental understanding and development of theories, which is essential for molecular design of polymer materials.
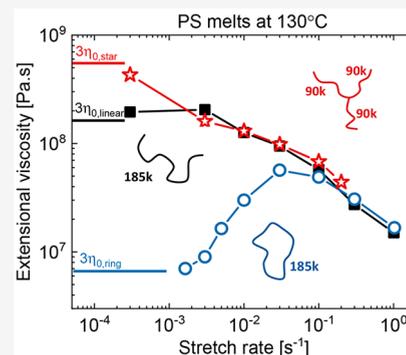
1. INTRODUCTION

Extensional flow is not only intimately relevant to polymer processing such as blow molding and fiber spinning but also very important for studying nonlinear rheology and dynamics of polymer liquids. Under a constant strain rate, the distance between two points in a simple shear flow increases linearly with time, while in a uniaxial extensional flow it increases exponentially with time. That means extensional flow is much stronger than shear flow. As a result, polymer chains align more effectively in extensional flow, leading to interesting and even unexpected rheological behavior.

However, compared with shear flow, studies on rheological behavior of polymer liquids in extensional flow are much less. This is largely due to the difficulties of measuring extensional rheology accurately and reliably in experiments. First, any no-slip boundary generates shear components; therefore, pure extensional flow is difficult to achieve. Second, in a well-defined experiment, it requires producing the extensional flow in a controlled way, for example, under a constant strain rate or a constant stress. This is not an easy task either, which we will address in the next section.

Along with the development of extensional rheometers, studies on extensional rheology of polymer liquids started growing rapidly, especially after the Sentmanat extensional rheometer (SER)[1] and the filament stretching rheometer (FSR) (with an online control scheme)[2,3] appeared around the year 2003. New experimental phenomena have been observed in extensional flow (e.g., refs 4−8) which challenge the traditional theories such as the classic tube model.[9] At the same time, the development of polymer chemistry enables synthesis of well-

defined complex macromolecular architectures,[10] making it possible to study the link between rheological behavior and molecular structures. In particular, combining extensional rheology with other experimental techniques such as small-angle neutron scattering (SANS) (e.g., refs 11−15) provides valuable insights into molecular conformations in extensional flow. Furthermore, with the progress of computer science including both hardware and algorithms, computer simulations become more and more important and have made significant contributions in fundamental understanding of polymer dynamics in recent years (e.g., refs 16−18).

With the aid of all the above-mentioned techniques across different disciplines, several important developments have been made in nonlinear rheology and dynamics for polymer systems. Because this Perspective is not a comprehensive review, we attempt to summarize and comment on the latest and most interesting achievements in this area. The rest of the Perspective is organized as follows. In section 2 we start with an introduction of experimental techniques to briefly discuss if the measurements of extensional rheology are reliable. Combining extensional rheology with other techniques is also introduced in this section. Then we summarize the latest important experimental
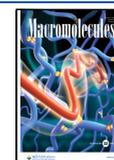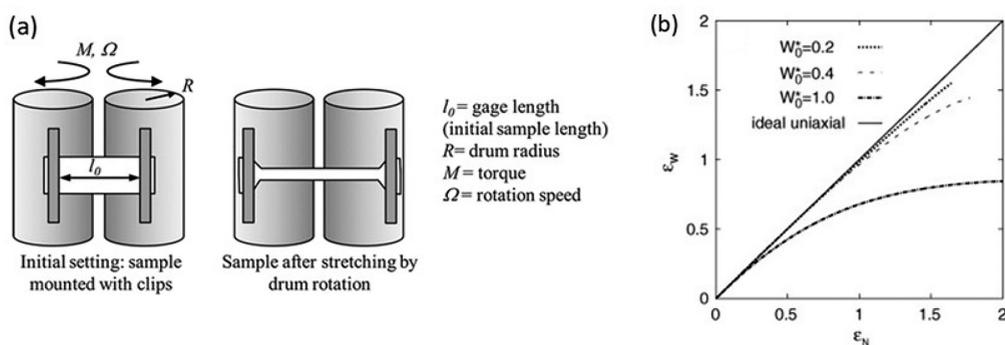
Figure 1. (a) Illustration of Sentmanat extensional rheometry. Reproduced with permission from ref 27. Copyright 2015 Elsevier. (b) Hencky strain based on the width of the sample as a function of the nominal Hencky strain (input strain rate multiplied by time) for a neo-Hookean polymer at different aspect ratios. Reprinted with permission from ref 28. Copyright 2010 Elsevier.
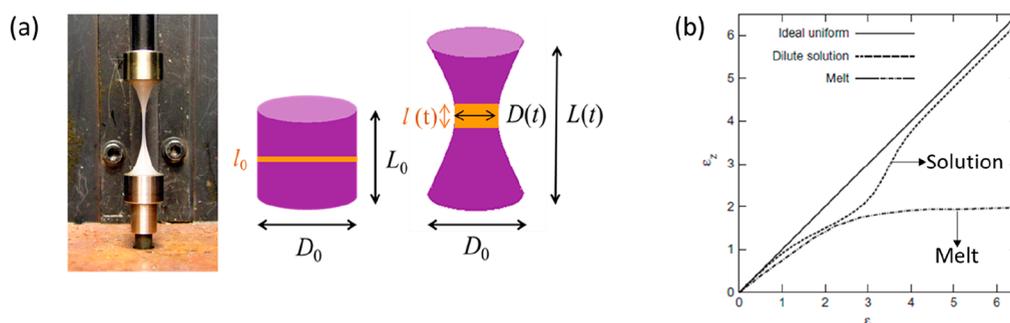
Figure 2. (a) Illustration of filament stretching rheometry. The photo shows a sample between a bottom and a top plate after filament stretching. (b) Typical curves of nominal Hencky strain based on the sample length (i.e., distance between the two plates) as a function of true Hencky strain based on the mid-diameter of the filament for polymer melts and solutions. Adapted with permission from ref 3.

findings for polymers with different macromolecular architectures in section 3. We also include some results of combining extensional rheology with small-angle neutron scattering in this section to further understand the rheological behavior. Finally, we conclude with highlighting open questions and challenges in this area and expand the topic of extensional rheology by discussing its influence on other areas such as liquid fracture and mechanical properties of polymers.

2. EXPERIMENTAL TECHNIQUES

2.1. State-of-the-Art Extensional Rheometers. There are different types of extensional rheometers developed during the past decades. Some typical examples include the rheometrics melt extensometer (RME),[19,20] the Münstedt tensile rheometer (MTR),[21] the Sentmanat extensional rheometer (SER),[1] the extensional viscosity fixture (EVF, very similar to SER, designed by TA Instruments), and the filament stretching rheometer (FSR).[2,3,22,23] While the above extensional rheometers directly measure the force (or torque) during stretching, there are other rheometers that do not. For example, the cross-slot extensional rheometer (CSER)[24] uses the stress-optical rule and measures the stress through birefringence patterns. It measures steady flow only but not the transient stress. A comparison of the experimental results from SER, FSR, and CSER can be found in ref 25, while a comparison of the results from EVF and FSR can be found in ref 26.

In this subsection, we focus on SER and FSR since SER is probably the most-used extensional rheometer today, while FSR (with an online control scheme) is so far the only extensional rheometer that can strictly control a constant strain rate at large

deformation over a Hencky strain of 7. The Hencky strain is defined as $\epsilon = \ln \lambda$, where $\lambda = l/l_0$ is the stretch ratio calculated from the initial sample length (l_0) and the length after stretching (l). If the sample is incompressible, the stretch ratio can also be calculated from the changes of other dimensions (e.g., widths and thicknesses).

SER was designed by Sentmanat in 2004.[1] Although called a rheometer, it is actually a fixture that can be easily accommodated onto a number of conventional rotational rheometers. Because of this versatility and simple manipulation, SER soon becomes a popular extensional rheometer. A very similar device, the extensional viscosity fixture (EVF) designed by TA Instruments after SER, is also widely used. As shown in Figure 1a,[27] SER contains dual wind-up drums rotating on the opposite direction to stretch polymer melts and elastomers which are stuck to the drums. The sample is assumed to undergo a uniform uniaxial extension with a constant Hencky strain rate when the drums rotate at a constant angular velocity. However, the deformation of the sample is not measured and sometimes does not follow the case as expected. To get an ideal uniaxial extension, SER has a general requirement that the aspect ratio of the sample, defined as $W_0^* = W_0/l_0$ where W_0 is the initial sample width and l_0 is the gage length (shown in Figure 1a), is smaller than 1. While this may work for many samples, there are still quite a few materials that show deviation from the ideal uniaxial extension with $W_0^* < 1$. For example, Figure 1b shows the result from a 3D finite element simulation for a neo-Hookean polymer.[28] The figure plots the Hencky strain ϵ_w based on the width of the sample as a function of the nominal Hencky strain ϵ_N which is simply the input strain rate multiplied by time. As

shown in Figure 1b, even with $W_0^* = 0.4$, there is an obvious deviation from the ideal uniaxial extension when the nominal Hencky strain is larger than 1. To ensure an accurate measurement, some researchers use cameras to record the changes of width and thickness of the samples to check if they follow the ideal case (e.g., ref 29).

SER can usually reach a maximum Hencky strain of 3.5−4.0. In many cases, this is not large enough for a polymer liquid to reach steady stress. Furthermore, it is reported that flow instabilities such as necking may happen during stretching.[30−32] To solve these issues, FSR with an online control scheme was developed in 2003[2,3] and then commercialized in 2015. As shown in Figure 2a, in FSR the sample is stretched vertically in-between the two plates. It initially has a cylindrical shape and then becomes a filament during stretching due to the no-slip condition at its two ends. FSR does not measure the whole sample since the deformation along the filament is not homogeneous. It only measures a thin layer at the middle of the sample (illustrated as the orange part in Figure 2a) which is close to an ideal uniaxial extension. The two ends with the no-slip condition may still influence the measurements of the middle layer at short time in the startup of the extensional flow, especially when the aspect ratio of the initial sample (defined as sample length divided by sample radius) is small. This can be improved by prestretching the sample before the measurements. Sometimes prestretching is also used for avoiding sample slipping off the end plates, since the force during stretching would be smaller with a smaller mid-diameter while the contact area at the two ends remains the same.

The length of the thin layer l cannot be measured directly; therefore, the Hencky strain ϵ is measured through the mid-diameter D by using a laser micrometer. To obtain a constant Hencky strain rate, it requires that D decreases exponentially with time. Figure 2b plots ϵ_z, defined as $\epsilon_z = \ln(L/L_0)$ where L is the distance between the two plates, as a function of Hencky strain ϵ. To reach a desired value of ϵ, the value of ϵ_z can vary a lot depending on different samples. That means before a measurement it is unknown how to separate the two plates so that a constant strain rate can be achieved at the midfilament plane. One way is to use trial and error to improve the route of separating the plates, known as the open-loop control scheme. But it usually requires three or more iterations for polymer melts, which wastes both time and samples. Therefore, a closed-loop control scheme is incorporated in FSR to control the movement of the plates instantaneously.[3] With this online control scheme, the evolution of the mid-diameter is strictly controlled even when necking happens. Thus, a maximum Hencky strain above 7 under a constant strain rate can be achieved. The operating principle of using the online control scheme has been validated in a recent simulation.[33] The accuracy of FSR has also been checked by comparing the results with SER, EVF, and CSER.[25,26]

While most extensional measurements are performed with a constant strain rate, in which the deformation history is clear and is convenient to compare the experimental data with model predictions, FSR can do more types of measurements which are also useful, including constant stress,[34] stress−relaxation,[35] reverse flow,[36] large-amplitude oscillation,[37] and planar extension.[38] For example, in steady flow, the extensional viscosity measured from a constant-strain-rate experiment should be the same as that measured from a corresponding constant-stress measurement. But in a constant-strain-rate experiment, steady flow is usually reached at large deformation

where the cross-sectional area of the sample is small, resulting in a small force, and the data could be very scattering especially at low rates. As shown by Alvarez et al.,[34] this could be greatly improved by constant-stress measurements where a steady flow is reached at a smaller strain. Another example is stress relaxation. As reported by Huang et al.,[39] a start-up of fast extensional flow with a constant strain rate cannot distinguish the two polystyrene melts with linear and star molecular architectures, but the two samples show an obvious difference in stress relaxation.

Both SER and FSR only use a small amount of sample in a measurement, typically around 40−120 mg. However, both have a problem with measuring samples with low viscosity, since gravitational sagging happens. Recently, a horizontal extensional rheometer combining the merits of SER and RME for low viscosity polymer melts was designed.[40] It is reported that this rheometer extends the low viscosity limit to about 2 decades compared with the SER fixture. Furthermore, Szabo et al.[41] reported constant-force measurements in extensional flow where the constant-force condition is achieved with gravity. This type of experiment allows measuring samples in a very strong extensional flow with fast strain rates and large strain which may beyond the range of SER and FSR with the control scheme.

2.2. Combining Extensional Rheometry with Other Techniques.
Rheological measurements cannot provide direct information about molecular conformations in a flow. To further explain the extensional rheological behavior on a molecular level, extensional rheometry is combined with other experimental techniques, usually scattering techniques such as small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS). They can provide quantitative results of the average molecular conformation with dimensions. An example is shown in section 3. An overview of SAXS and SANS can be found in a recent primer.[42]

For *ex situ* scattering measurements, a polymer sample is first stretched in an extensional rheometer. As soon as the flow stops, the sample is immediately quenched below its glass transition temperature to keep the molecular conformation. Then in the next step, the quenched solid sample is measured with X-ray or neutron beams. Figure 3a shows the photos of some quenched polystyrene filaments. To increase the scattering intensity, here
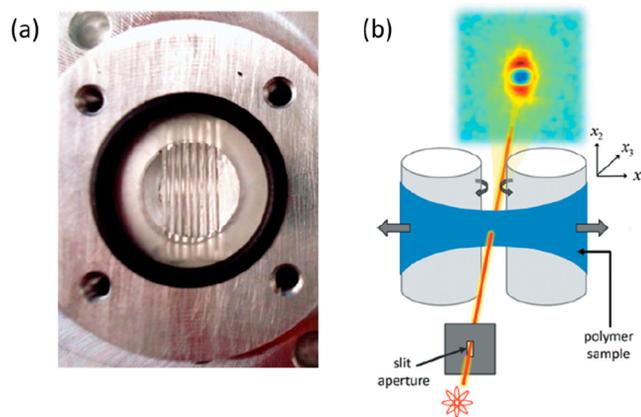
Figure 3. (a) Uniform part of each filament placed parallelly on a sample holder for *ex situ* SANS measurements. (b) Illustration of *in situ* SANS based on an SER. Reproduced with permission from ref 13. Copyright 2017 American Institute of Physics.
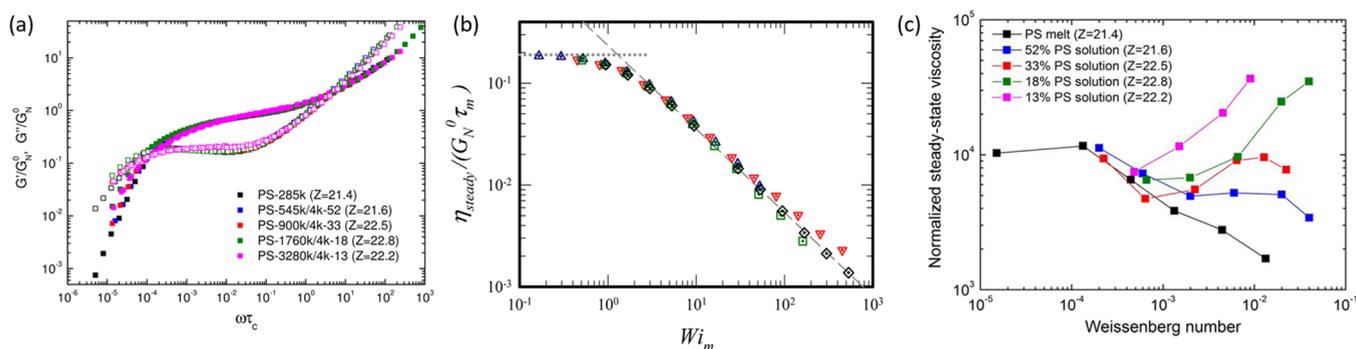
Figure 4. (a) Normalized storage modulus G' and loss modulus G'' as a function of normalized angular frequency for PS solutions with different polymer fractions (from 13% to 100%) but similar number of entanglements. Reproduced with permission from ref 7. The τ_c in the figure is from a model other than the tube model, but it is equivalent to τ_e as explained in ref 6. (b) Normalized steady-state viscosity as a function of Weissenberg number in shear flow for two pairs of PS melts and solutions with Z = 10 and 13.9. Reproduced with permission from ref 50. (c) Normalized steady-state viscosity as a function of Weissenberg number in extensional flow for four PS solutions and a PS melt with similar number of entanglements (the same samples in (a)). Reproduced with permission from ref 7.

several filaments were stretched and quenched under identical conditions. Then the uniform part of each filament was cut and placed parallelly on a sample holder for SANS measurements.

Ex situ scattering is easier and more convenient to carry out compared with *in situ* scattering. However, if the quench cooling rate is not fast enough, it gives an opportunity for the aligned molecules to relax. Furthermore, if the glass transition temperature of the polymer is below room temperature, *ex situ* scattering is not a suitable way. Therefore, several homemade experimental setups, usually based on SER (Figure 3b)[13,43,44] but recently also based on FSR,[45] have been developed for *in situ* scattering measurements.

Besides experimental techniques, nowadays computer simulations such as molecular dynamics (MD) simulations play a more and more important role in the fundamental understanding of rheological behavior and dynamics of polymer systems. We include some examples in the next section.

3. EXTENSIONAL RHEOLOGY AND DYNAMICS OF POLYMERS WITH DIFFERENT MOLECULAR ARCHITECTURES

3.1. Linear Polymers. Although linear polymers have the simplest molecular architecture, their nonlinear behavior in extensional flow is still not fully understood and open questions remain. In this subsection we focus on the topic of flow-induced reduction of segmental friction which has become a key concept in recent years. For details of theoretical views on this subject, we recommend reading the Perspective by Ianniruberto et al.[46] and the Review by Matsumiya and Watanabe,[47] both published very recently. Here we recall the related experimental results and arguments, with our comments mainly from an experimental point of view.

Linear Polymer Systems with the Same Z but Different N_e. For entangled linear chains, one of the basic questions is, how many parameters are needed to describe their rheological behavior? According to the tube model,[9] there are three basic parameters: the number of entanglements per chain (Z), the number of Kuhn segments per entanglement strand (N_e), and the relaxation time of one entanglement strand (τ_e). The other important parameters, such as reptation time (τ_d), Rouse time (τ_R), and plateau modulus (G_N^0), are related to these three parameters.

We first take a look at samples of the same chemistry with the same number of entanglements per chain (Z) but with different

concentrations. With lower concentration, the entanglement molecular weight is larger, hence the larger N_e. For this system, the rheological behavior in the linear regime can indeed be described with the three basic parameters as shown in Figure 4a.[7] In this figure a series of polystyrene (PS) solutions with different polymer fractions (from 13% to 100%) but similar number of entanglements ($Z \approx 22$) show identical linear viscoelasticity when plotting their normalized storage modulus G' and loss modulus G'' (normalized with G_N^0 which is related to N_e) as a function of normalized angular frequencies (normalized with $1/\tau_e$). This identical behavior with the same Z in the linear regime has also been demonstrated for polymer systems with different chemistry.[48,49] Furthermore, the three basic parameters can also describe the nonlinear rheology in shear flow. Figure 4b[50] shows the identical shear-rate thinning behavior for several PS melts and solutions by plotting the normalized steady-state viscosity as a function of normalized shear rate (Weissenberg number).

From the results in Figures 4a and 4b, it seems that, providing the same Z, polymer melts and solutions should also have the identical extensional rheology in normalized plots, but experimental results are not as expected. Figure 4c plots the normalized steady-state viscosity in extensional flow as a function of normalized Hencky strain rate (Weissenberg number) for the same samples in Figure 4a. In contrast with Figure 4b, the samples in Figure 4c do not have the similar nonlinear behavior especially at fast strain rates—it changes from extensional rate thinning for the highest concentration (the melt) to extensional rate thickening for the lowest concentration.

One possibility to explain the different rheological behavior of the PS melts and solutions in extensional flow is the finite extensibility of the chains. In shear flow, chain orientation (i.e., the alignment of entanglement segments) dominates, but in extensional flow, chain stretch (i.e., the alignment of Kuhn segments) has a large influence. With a smaller value of N_e for solutions with higher concentrations, the maximum chain stretch ratio, defined as $\lambda_{max} = \sqrt{N_e}$, is also smaller. This may limit strain hardening and thus result in a lower normalized steady-state viscosity.

The above PS melts and solutions all have the same chemistry (the solvents are styrene oligomers that also have the same chemistry). It has been reported recently that pure melts of
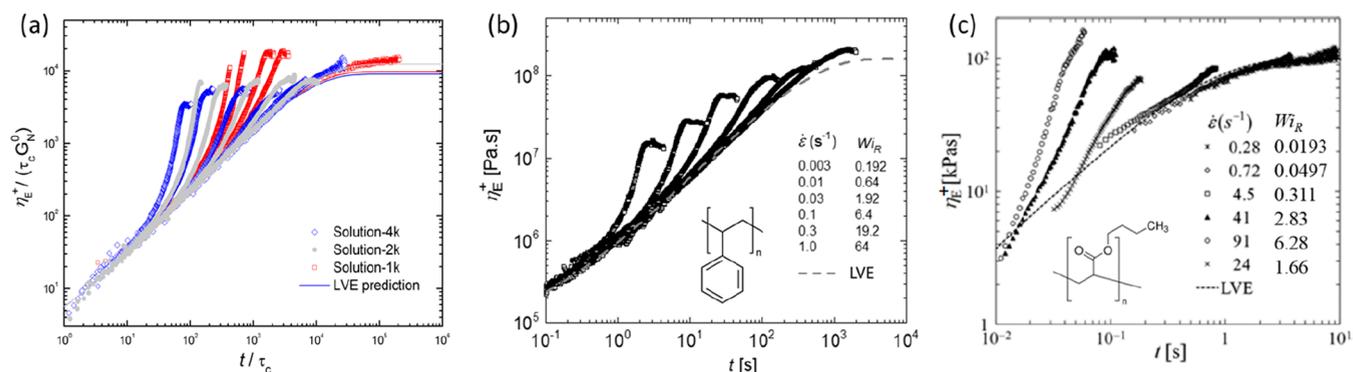
Figure 5. (a) Normalized extensional stress growth coefficient as a function of normalized time for three PS solutions with the same concentration but different oligomeric solvents. Adapted with permission from ref 61. The τ_c in the figure is from a model other than the tube model, but it is equivalent to τ_e as explained in ref 6. (b) Extensional stress growth coefficient as a function of time for a 185 kg/mol PS melt at 130 °C. Adapted with permission from ref 8. (c) Extensional stress growth coefficient as a function of time for a 200 kg/mol PnBA melt at 21.5 °C. Adapted with permission from ref 64.

different chemistry but with the same Z also show different rheological behavior in extensional flow. For example, three polymer melts—polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(*tert*-butylstyrene) (PtBS)—were measured by Morelly et al. in extensional flow.[49] The PtBS, which has the largest side-group in chemical structure, shows more strain hardening compared with the other two melts, while the PMMA, which has the smallest side-group, shows less strain hardening than the other two. Because the bulky side-groups act as "solvents" and lead to larger values of N_e, it seems that the difference in strain hardening can also be attributed to different λ_{max}, which is similar as the case for PS solutions with different concentrations.

However, theories explain the above results in different ways. Ianniruberto[51] shows that finite extensibility alone is insufficient to describe the data in Figure 4c; flow-induced friction reduction effects must be considered. The idea of flow-induced friction reduction was proposed by Ianniruberto et al.[52,53] and Yaoita et al.[54] It says that when the Kuhn segments are aligned in a strong flow, the segmental friction coefficient decreases, while in convention it was assumed to be constant. In other words, the relaxation time τ_e may be shorter in a flow compared with the value in equilibrium. This idea can also explain the case for melts with different chemistry: the segments with smaller side-groups (e.g., PMMA) are easier to be aligned, leading to more friction reduction and thus weaker strain hardening. By contrast, the extended interchain pressure (EIP) model developed by Wagner and co-workers, which does not incorporate the idea of friction reduction, also captures the different behavior of PS melts and solutions as well as melts with different chemistry mentioned above.[55−57] The EIP model assumes that the chain stretch is limited by the interchain tube pressure (in the lateral direction of a tube segment) which depends on the concentration. In a recent experiment also on PS solutions by André et al.,[58] it is reported that the extensional steady-state viscosity shows an unexpected dependence on the concentration, which can be explained in the framework of friction reduction, but still does not exclude other explanations as stated by the authors. The EIP model can also describe these data well.[59] Furthermore, MD simulations for steady extensional flow and stress relaxation of highly aligned chains by using a Kremer−Grest bead−spring model do not find direct evidence of friction reduction,[16,17] while recently another bead−spring simulation shows that friction reduction occurs under strong flows.[60]

Linear Polymer Systems with Both the Same Z and N_e. From an experimental viewpoint, it would be clearer to show if an extra parameter or another mechanism is needed by comparing systems with the same Z and same N_e. When N_e is the same, the effect of different τ_e (determined from the equilibrium state) for different samples can always be eliminated by normalization as mentioned above, assuming time−temperature superposition (TTS) holds. On the other hand, τ_e can also be adjusted to the same value by selecting proper temperatures, that is, at the same distance from their glass transition temperature T_g.

The first comparison for samples with both the same Z and N_e was performed by Huang et al.[61] Three PS solutions, diluted from the same PS (545 kg/mol) into the same concentration (52%) but with different solvents, were measured in extensional flow. The solvents are oligomeric styrene (OS) with molecular weights of 1, 2, and 4 kg/mol, all far below the entanglement molecular weight (13.3 kg/mol). Surprisingly, the three solutions still behave differently in extensional flow even with the same N_e (thus the same λ_{max}). As shown in Figure 5a, the solution with the 1K solvent shows obviously more strain hardening compared with the other two. But this difference seems to disappear when the OS is above a critical molecular weight. As reported by Shahid et al.,[62] the samples containing 10% long PS chains (820 kg/mol) and 90% short chains with molecular weights of 72K, 34K, 23K, and 8.8K reach the same extensional steady-state viscosity when the Rouse time-based Weissenberg number $Wi_R > 1$ (as long as the matrix is not stretched). This behavior is captured by the EIP model.[63] In Figure 5a, the behaviors of the solutions with 2 and 4 kg/mol OS are also very close to each other.

Such different rheological behavior is observed for different melts with the same Z and N_e as well. According to Sridhar et al., poly(*n*-butyl acrylate) (PnBA) melts and PS melts have close values of λ_{max} (4.1 and 4.2, respectively)[64] and thus similar N_e. Figures 5b and 5c plot the extensional stress growth coefficient (transient viscosity) as a function of time for a 185 kg/mol PS melt[8,50] and a 200 kg/mol PnBA melt,[64] respectively, both with $Z \approx 13$. In Figure 5b, the plateau part of each curve (i.e., steady-state viscosity) for the PS melt decreases monotonically with increasing stretch rate (i.e., extensional rate thinning) even when the Rouse time-based Weissenberg number $Wi_R > 1$. By contrast, the PnBA melt in Figure 5c shows significant strain hardening when $Wi_R > 1$, leading to extensional rate thickening. It should
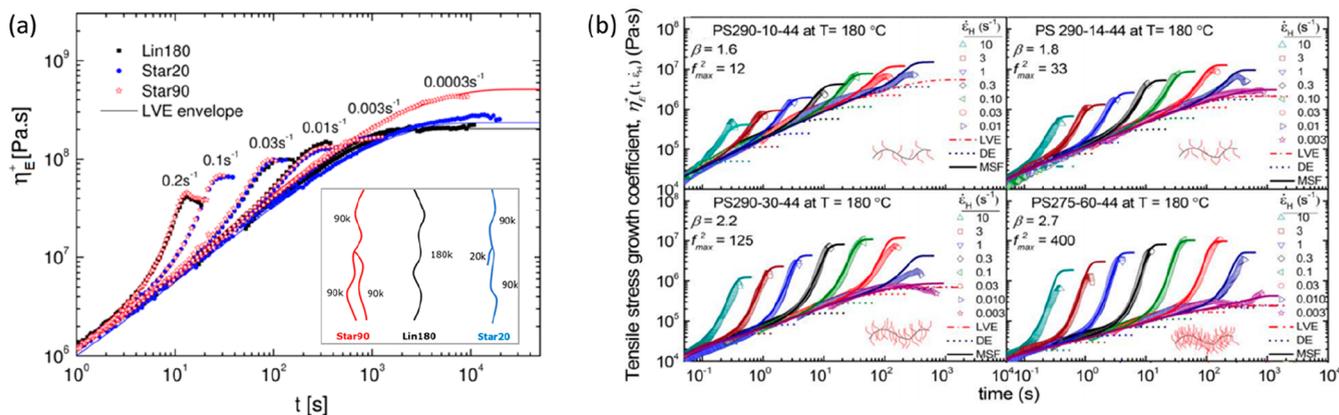
Figure 6. (a) Extensional stress growth coefficient as a function of time at 130 °C for three PS melts with molecular architecture of linear, 3-arm asymmetric, and symmetric star. All the molecules have the same span length. Adapted with permission from ref 39. The inset illustrates the hypothesis of the molecular conformation in fast steady extensional flow. (b) Extensional stress growth coefficient as a function of time at 180 °C for four comb PS melts. The molecules have the same molar mass of both backbone and arms but different numbers of arms. Adapted with permission from ref 83.

be noted that while Wingstrand et al. show that a PMMA solution and a PS melt with the same Z and N_e behave identically in extensional flow,[48] the authors also claim that the molecular weight of the oligomeric solvent influences the behavior of the PMMA solution, similar to the case in Figure 5a.

The experimental results in Figure 5 directly show that λ_{max} alone is insufficient to explain the difference. Figure 5a can be explained with the idea of friction reduction by considering that in fast extensional flow the short oligomer chains are aligned by the long polymer chains with nematic effects.[65] The 4 kg/mol solvent is easier to be aligned compared with the 1 kg/mol solvent, thus resulting in more friction reduction and therefore lower steady-state viscosity. For melts with different chemistry in Figures 5b and 5c, the bulky side-groups may serve as "solvents" as mentioned previously. Compared with PS, PnBA has more flexible side-groups which are more difficult to be aligned, therefore leading to less friction reduction. Primitive chain network simulations with friction reduction successfully capture the extensional behavior of PnBA and PS melts.[66] With regard to the EIP model, it can also describe the different behavior in Figure 5a by adding an extra mechanism that oligomeric solvents with molar mass smaller than a critical value (a quarter of the entanglement molar mass) are less effective transmitters of interchain pressure.[56] However, the EIP model cannot describe the case in Figure 5c since it does not predict an extensional rate thickening for well-entangled monodisperse linear melts at Wi_R > 1. Very recently, Wagner and Narimissa proposed a new constitutive equation based on enhanced relaxation of stretch (ERS).[67] The stretch evolution equation of the ERS model can be expressed in terms of monomeric friction reduction and provides analytical and parameter-free relations of monomeric friction reduction as a function of chain stretch. This new model captures the rheological behavior of PS melts and solutions but still needs further validation especially for polymer melts with different chemistry.

While the concept of friction reduction seems to be more promising, there are several issues requiring further clarification in experiments in our view. For example, it is mentioned above that comparison under normalization as shown in Figure 5a assumes that TTS holds for the samples. Although not reported in the original paper,[61] the Solution-1k in Figure 5a was tested at two temperatures of T_g + 36 °C and T_g + 41 °C, and TTS was found to be valid. André et al. also claimed that TTS works well

for PS solutions (with 9 kg/mol OS as solvents) in the nonlinear regime in extensional flow at T_g + 23.4 °C and T_g + 28.4 °C.[58] However, breakdown of TTS in fast extensional flow for similar PS solutions in a wider temperature range from T_g + 25 °C to T_g + 55 °C has been reported recently by Yuan et al.[68] Furthermore, while PS and OS with the same chemistry are assumed to be perfectly miscible, simulations show that flow-induced phase separation may happen even in the case that all the constituents have the same chemistry.[69,70] Therefore, whether the different rheological behavior in Figure 5a is due to phase separation requires further investigation. With regard to the melts with different chemistry, while the very different behavior of extensional rate thinning and extensional rate thickening (Figures 5b and 5c) is useful for validating models, experimental data of melts with extensional rate thickening are very limited, and more measurements are desired. In addition, it is reported that effect of hydrogen bonding is difficult to avoid in PnBA melts.[71]

A simpler case to test the idea of friction reduction is to measure unentangled melts in fast extensional flow. Such experiments were performed for unentangled PS and PtBS melts with similar number of Kuhn segments by Matsumiya et al.[72] The authors show that a model with finite extensible nonlinear elasticity (FENE) alone cannot describe the data, and friction reduction must be incorporated to capture the behavior. Simulations also show that friction reduction needs to be considered to match the data.[73] However, Narimissa and Wagner show that a single integral constitutive equation based on the Rouse model with a finite conformational stretch parameter can also describe the data reasonably.[74] From an experimental viewpoint, the two unentangled melts with similar number of Kuhn segments have already shown different behavior in extensional flow, which is a sign that an extra mechanism may be needed. However, the difference is not significant enough (compared to the cases in Figures 5b and 5c) to distinguish different models, and thus experiments on more unentangled melts are desired. On the other hand, as suggested by Ianniruberto et al.,[46] atomistic molecular dynamics simulations of unentangled melts for different chemistry would be useful to determine how sensitive the friction reduction is to chemical details. Scattering experiments for quantification of molecular conformation changes at the monomer level would also be very interesting to determine
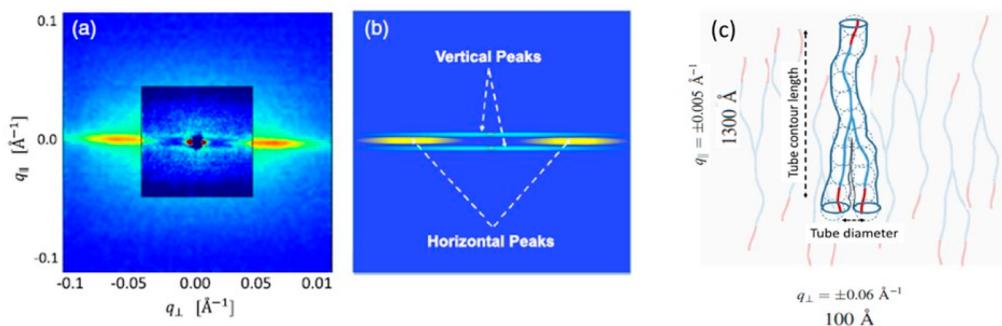
Figure 7. (a) 2D SANS pattern for the 3-arm symmetric star PS melt quenched from a fast steady-state extensional flow. Each arm has a molar mass of 102 kg/mol, with a small deuterated part (7.7 kg/mol) at each arm end. (b) Illustration of the characteristic peaks of the 2D SANS pattern in (a). (c) Illustration of the molecular conformation of the highly aligned star molecules in fast steady-state extensional flow based on the analysis of the 2D SANS patterns shown in (a). Figures adapted with permission from ref 14.

the roles of side-groups for melts with different chemistry in nonlinear rheological response in extensional flow.[75]

Effect of Molecular Weight Distribution. The above systems mainly concern model polymers with a narrow molecular weight distribution (MWD), and the dispersity is typically smaller than 1.1. While the model polymers are useful for studying the dynamics and comparing with models, most polymers used in the industry have a broad MWD. Tuning of MWD is frequently used to attain optimum strain hardening. As already studied in earlier works by for example Minegishi et al.[76] and Nielsen et al.,[77] it has been found that mixing a small amount of long chains into a matrix of much shorter chains leads to enhanced strain hardening. The results were also studied in modeling and simulations as reported by Wagner et al.[78] and Takeda et al.[79] These studies show that the long chain stretch dominates the stress at the strain hardening, which agrees with the recent work by Shahid et al.[62] Together with the results from model polymers shown above, we can make a summary that the strain hardening is mainly influenced by N_e—a larger value of the average N_e of the system leads to a more significant strain hardening. The zero-shear-rate viscosity can be increased by increasing the average Z of the system. While the stress is dominated by the long chain, using longer chains does not necessarily increase the strain hardening, as the zero-shear-rate viscosity also increases. It is also observed that some linear PS melts with a broad MWD show strain hardening at very low strain rates, leading to a strain rate thickening of extensional viscosity before showing the thinning behavior (e.g., ref 80), which is not observed for well-entangled monodisperse linear PS melts. However, this is often observed for branched polymers, as we show later in Figure 6b for the comb PS. In the case of branched polymers, the chain segments in between the two neighboring branch points are easier to be stretched, which could be the reason for strain hardening at low rates. Similarly, for such strain hardening observed in linear PS, it could also be due to the fact that the chain segments in the long chains are easier to be stretched compared with the average relaxation time of the system.

3.2. Branched Polymers. The extensional rheology of linear polymer melts and solutions has already shown complexity that it depends not only on the three tube parameters but also on the chemistry of the monomers as well as solvents. To investigate the influence of macromolecular architecture, it is thus reasonable to compare polymer melts with the same chemistry. On the synthesis side, although it is possible to synthesize model polymers with well-controlled architectures, it

is not an easy task, and usually only a small amount of material is available for rheological measurements. Therefore, compared with linear polymers, experimental data of branched model polymers in extensional flow are very limited, especially in steady-state extensional flow where large deformations are required.

On the basis of the limited data of extensional steady stress of an asymmetric star PS melt and a pom-pom PS melt,[81] Ianniruberto and Marrucci pointed out that the branched PS behaves like linear PS in fast steady-state extensional flow.[82] This finding is very interesting because it shows that melts with very different zero-shear-rate viscosity may have the same extensional viscosity. Subsequently, Huang et al.[39] measured the extensional rheology of three PS melts with linear, 3-arm asymmetric star, and 3-arm symmetric star architectures. The three different molecules have different molecular weights but the same span length; that is, the largest contour length from one chain end to another end is the same. As shown in Figure 6a, although the three PS melts have different zero-shear-rate viscosities, their rheological behavior in extensional flow is identical when stretched faster than the inverse Rouse time (>0.01 s^{-1} in the figure), in agreement with the findings from Ianniruberto and Marrucci. The hypothesis is that in a fast extensional flow the star molecules are highly aligned and thus have a similar conformation as the linear molecules, as shown in the inset of Figure 6a.

Star polymers have the simplest branched architecture with one branch point only. When the branch points are increased to two or more, situations become complicated because many factors such as molecular weight of arms and backbones, number of arms, and details in architecture (e.g., pom-pom, comb, and dendritic) can influence rheological behavior. Abbasi et al.[83] investigated a series of comb PS melts with the same backbone of 290 kg/mol and the same arms of 44 kg/mol ($Z \approx 3$) but different number of arms. The zero-shear-rate viscosity is usually increasing with increasing branch points. However, with the same backbone, the molecular weight of the strand between neighboring branch points is decreasing with increasing branch points; when it is decreased to smaller than the arm length, the zero-shear-rate viscosity starts to decrease, since the arms become more and more difficult to get entangled. As shown in the linear viscoelastic (LVE) envelopes (red dashed line) in Figure 6b, when the number of arms increases from 10 (top-left panel) to 60 (bottom-right panel), the zero-shear-rate viscosity drops more than 10 times. The extensional measurements in Figure 6b did not reach steady state. However, in the measured
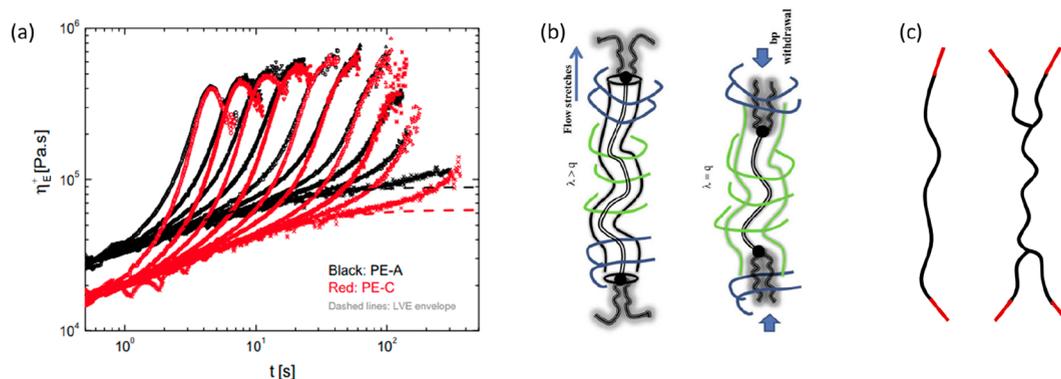
Figure 8. (a) Extensional stress growth coefficient as a function of time at 150 °C for two PE melts. Reproduced with permission from ref 26. Copyright 2016 Springer. (b) Illustration of the concept of branch point withdrawal. Adapted with permission from ref 84. (c) Illustration of molecular architectures that would be interesting to be stretched and measured in SANS. The red parts represent the deuterated parts.
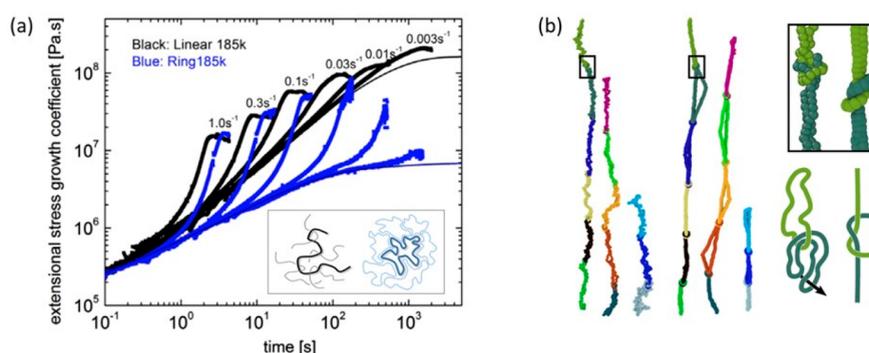
Figure 9. (a) Extensional stress growth coefficient as a function of time at 130 °C for a linear and a ring PS melt, both with molecular weight 185 kg/mol. Adapted with permission from ref 8. The inset illustrates the molecular conformation in equilibrium. (b) Illustration of the flow-driven formation of topological links that connect multiple rings based on the results of molecular dynamics simulation. Adapted with permission from ref 18.

range of deformation, it is interesting to see that at a same stretch rate the extensional stress reaches very similar level for the four samples, despite a big change in zero-shear-rate viscosity. This observation also suggests that when the molecules are highly aligned, the extensional stress is more influenced by the span length of the molecules.

The hypothesis that branched polymers are highly aligned in fast extensional flow and thus have a similar conformation as linear polymers has been confirmed in SANS by Mortensen et al.[14] for a 3-arm symmetric star PS. The star PS is very similar as the one in Figure 6a, with a small part at each arm end deuterated. The sample was stretched in a fast steady extensional flow and then quenched for *ex situ* SANS. Figure 7a shows the 2D SANS pattern, and Figure 7b highlights the characteristic peaks. The two vertical peaks which are close to each other show a long characteristic length along the flow direction. With further analysis of the SANS data, it can be obtained that this characteristic length is about 1300 Å, which is in between the theoretical lengths when the star is fully oriented along flow (1040 Å) and when the star is fully stretched (4960 Å). The two horizontal peaks show a short characteristic length perpendicular to the flow direction, which is roughly 100 Å after analysis. This length is close to the tube diameter 85 Å.[14] Hence, the conformation of the molecule is obtained as illustrated in Figure 7c, which is indeed highly aligned: The long length (1300 Å) is the distance between the two arm ends along the flow direction, and the short length (100 Å) is the distance between the two arm ends perpendicular to the flow direction. Very recently,

Mortensen et al.[15] also confirmed the different relaxation stages of the highly aligned star PS from chain retraction to configurational relaxation in SANS.

The above results are important because they provide a guidance for molecular design of branched polymers: the zero-shear-rate viscosity can be tailored by the number and length of arms, while the extensional viscosity in fast flow can be controlled by span molecular weight. Furthermore, Shahid et al.[62] have shown that for bidisperse linear PS blends with long and short chains the steady extensional viscosity is determined by the long chains, while the length of the short chains only influences the transient strain hardening, which is similar to the case shown in Figure 6b for comb PS. The findings allow the design for polydisperse systems with more complex architectures. Figure 8a shows an example of two commercial polyethylene (PE) melts with different zero-shear-rate viscosity but identical extensional stress at large deformations in fast extensional flow.[26]

In Figure 8a, when the stretch rate is fast enough, the transient extensional stress does not increase monotonically with strain; a stress overshoot is observed. Such stress overshoot has also been observed in several commercial PE melts[5,25,26,84] and a model pom-pom PS melt.[81] The mechanism of the stress overshoot is still not clear, but the hypothesis is that disentanglement of arms happens when the molecules are highly aligned, leading to retraction of the backbone (i.e., branch point withdrawal) as illustrated in Figure 8b.[5,84] Primitive chain network simulations for pom-pom polymers reveals that branch point withdrawal is
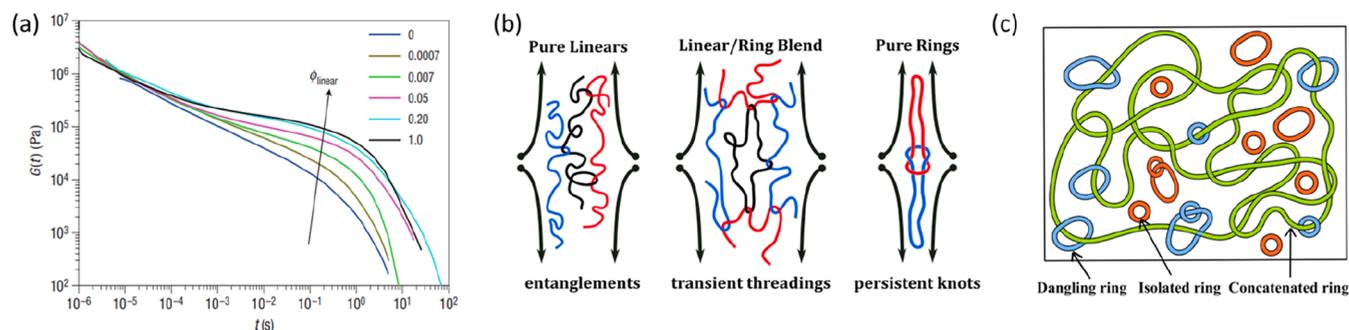
Figure 10. (a) Stress–relaxation modulus $G(t)$ for the mixtures of ring and linear molecules, both with molar mass of 198 kg/mol, at the reference temperature of 170 °C. The legend shows the fraction of the linear molecules. Adapted with permission from ref 86. (b) Illustration of molecular conformations and topological links in extensional flow for a pure linear melt, a pure ring melt, and a linear/ring blend. Reproduced with permission from ref 87. (c) Illustration of molecular conformations and topological links of a polymer system containing ring molecules in equilibrium. Reproduced with permission from ref 90.

the dominant mechanism for the backbone relaxation under flow.[85] Following the method in Figure 7, this hypothesis could be confirmed in SANS for an H-shaped or pom-pom PS melt with deuterated part at the end of each arm, as illustrated in Figure 8c. If backbone retraction happens, the characteristic length along the flow direction after the stress overshoot should be shorter than that at the stress maximum. A linear PS chain with the same span molecular weight (Figure 8c) could also be interesting to measure in SANS for comparison.

3.3. Ring Polymers. The molecular architecture of ring polymers is also very simple and maybe even simpler than linear polymers. However, their rheological behavior is very different from linear polymers already in the linear rheological regime. As illustrated in the inset of Figure 9a, without free chain ends, nonconcatenated ring molecules cannot be entangled as the linear chains, resulting in a much lower zero-shear-rate viscosity.[86] As seen from the LVE envelopes in Figure 9a (solid lines), the zero-shear-rate viscosity of the 185 kg/mol ring PS melt is more than 10 times lower compared with the 185 kg/mol linear PS melt.[8] Because of this special conformation of rings in equilibrium, the hypothesis was that in extensional flow they only show strain hardening at much faster strain rates compared with the linear melts. From the results of branched polymers that the span molecular weight determines the extensional viscosity in fast flows, it seems also reasonable to make the hypothesis that the extensional viscosity of ring melts is identical with the linear melts with half molecular weight of the rings.

However, recent experiments gave unexpected results.[8] As shown in Figure 9a, first, the ring PS shows significant strain hardening even at low strain rates compared with the linear PS. Second, in fast extensional flow (strain rates faster than 0.03 s⁻¹ in the figure), the ring PS reaches the same steady extensional viscosity with the linear PS that has the same molecular weight but larger span length. This interesting but confused behavior has been recently explained in MD simulations. O'Connor et al.[18] show that in extensional flow the ring molecules can form special topological links that connect multiple rings into a long chain, as illustrated in Figure 9b. These highly aligned long chains contribute to the significant strain hardening and large extensional viscosity of the ring melt. According to the simulations, it could happen that more than two rings are connected into a chain, and in the sample only a small percentage of the rings are connected. That means the same extensional steady viscosity of the ring and linear PS melts as

observed in Figure 9a should be a coincidence. To the best of our knowledge, the data in Figure 9a are the only experimental data so far for pure nonconcatenated ring polymers measured in steady extensional flow. Measurements for nonconcatenated rings with other molecular weight are thus desired. It would also be interesting to figure out if the topological links shown in Figure 9b can still form for rings with low molecular weight.

It has been reported that the rheology of ring polymer melts is extremely sensitive to linear contaminates[86]—the relaxation modulus shows an obvious change even with 0.07% linear molecules as shown in Figure 10a. As making pure non-concatenated rings is not an easy task in synthesis, using rings as additives seems to be a more realistic approach. Compared with pure linear chains and pure ring molecules, linear/ring blends can form new topological interactions by threading, as illustrated in Figure 10b. The rheological behavior of linear/ring blends can thus be tailored by changing the fraction of the constituents as well as changing the molecular weight of both linear and ring molecules. Preliminary work of extensional rheology combining with MD simulations and SANS measurements for a linear/ring blend shows that the threading–unthreading transition happens in extensional flow, leading to a stress overshoot similar as observed for branch polymers.[87] Nonlinear rheology in both shear and extensional flows for some more linear/ring blends has been reported recently by Parisi et al.[88] But both experimental and simulation data for linear/ring blends in extensional are still very limited. On the other hand, besides linear/ring blends, concatenated rings are also much easier to get compared to nonconcatenated rings, while their rheological/mechanical properties could be interesting as well. It is reported that polydimethylsiloxane (PDMS) elastomers prepared without cross-linking show excellent extensibility,[89] and recently Hu et al.[90] confirm that the unexpected elasticity of these elastomers originates from concatenated rings, as illustrated in Figure 10c.

4. CONCLUSIONS AND OUTLOOK

We have summarized the latest important experimental findings in extensional rheology, mainly for nearly monodispersed model polymer systems with well-controlled architectures, as they are useful for understanding polymer dynamics and validating different models. Although these model polymers have simple macromolecular architectures such as linear, ring, star, and comb, their rheological behavior in extensional flow is not simple, and open questions remain. The concept of flow-induced friction reduction for linear polymers, the idea of

retraction of backbones for branched polymers, and dynamics of linear/ring blends with different fractions all require further investigation. We did not include associative polymers in this Perspective. Their extensional rheology is also very interesting but more challenging. As reported by Yang et al.,[91] even for unentangled associative polymers, their rheological behavior in extensional flow may change dramatically by changing the strength of associating bonds. Much more possibilities can be explored by introducing associating bonds into entangled polymer systems with different macromolecular architectures. Similarly, block polymers[92] and polymer composites are two other large groups where extensional rheology could be interesting but challenging. Extensional measurements of polymer composites (e.g., refs 93 and 94) are difficult due to enhanced instability. This problem has been theoretically discussed recently by Yamamoto et al.[95]

Extensional rheology also has a big influence on other areas. When the stretch rate is fast enough, elastic fracture of polymer liquids is observed and demonstrated to depend on molecular parameters of the polymers but not on pre-existing micro cracks.[96,97] Experimental studies on liquid fracture are so far based on combining extensional measurements of critical stress and strain at fracture with high-speed imaging of crack propagation. However, the molecular mechanism of liquid fracture, e.g., if it is caused by scission of the polymer chains and if the chains are stretched to their theoretical maximum stretch ratio, still needs further investigation. Flow-induced crystallization is another area that has gained a lot of attention (e.g., refs 98 and 99). This phenomenon appears more effectively in extensional flow and often studied by combining extensional rheometry with *in situ* SAXS as shown in Figure 11.[98] Without
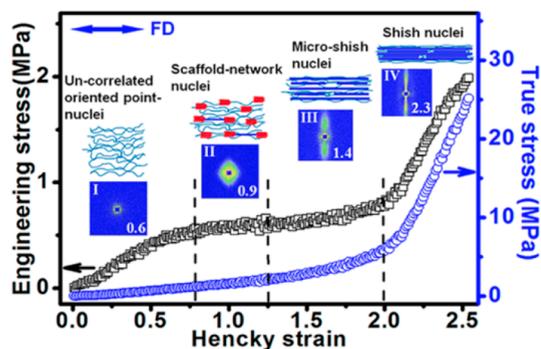
Figure 11. Extensional stress as a function of Hencky strain combining with 2D patterns of *in situ* SAXS for a high-density polyethylene melt. Reproduced with permission from ref 98.

flow-induced crystallization, quenching polymer melts from fast extensional flow may also change their crystallization since the polymer chains are highly aligned, as reported by Wingstrand et al.[100] For amorphous polymers, extensional rheology also influences their mechanical properties a lot. As shown in Figure 12,[101] while PS is usually a brittle material at room temperature, it becomes flexible when the melt is stretched in fast extensional flow followed by quenching. The resulting anisotropic PS also shows larger stress and strain at fracture in tensile tests at room temperature compared to the normal isotropic PS.

As discussed above, more data from both experiments and simulations will improve our understanding of extensional rheology and dynamics. This is essential for developing theories
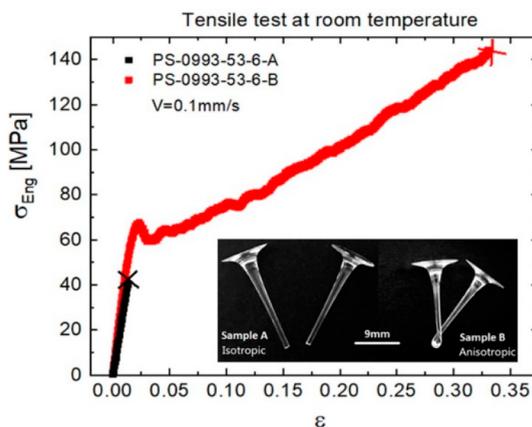
Figure 12. Engineering stress as a function of engineering strain from tensile tests at room temperature for two PS samples. The inset shows the photo of the same samples in bending. Adapted with permission from ref 84.

which provide a guidance for molecular design of more complexed polymer systems for a wide range of applications.
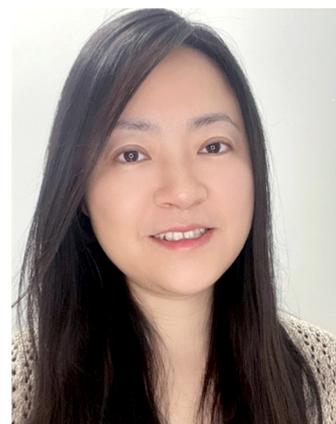
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Notes

Biography

Qian Huang received her B.E. from Zhejiang University in China in 2004 and her M.Sc. from the Technical University of Denmark (DTU) in 2006, both in Polymer Engineering. She was then working as a chemical process engineer in Shanghai until the end of 2009. She received her Ph.D. in molecular rheology of complex fluids also from DTU in 2013, under the supervision of Professor Ole Hassager. She continued working at DTU as a postdoc and later a researcher until 2020. In March 2021, she joined the Polymer Research Institute, Sichuan University in China, as a professor. Her research interests include the extensional rheology and dynamics of polymer melts and solutions with different macromolecular architectures, the mechanism

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