

Flow-Driven Stretch Fluctuations Govern the Nonlinear Viscoelasticity of Elongating Associative Polymer Networks

Songyue Liu¹ and Thomas C. O'Connor¹

Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA



(Received 15 April 2025; accepted 6 August 2025; published 28 August 2025)

We use nonequilibrium molecular dynamics simulations to verify recent tube-model predictions that associative polymer networks exhibit broad stretch fluctuations during elongational flow. Simulations further show that these fluctuating dynamics give rise to the rate-dependent extensional viscosity η_E measured in filament stretching experiments on H-bonding networks. Simulations model bivalent associative networks with a reactive bead-spring model for varying association strength and extensional strain rate. We observe that stretch fluctuations are driven by a new form of chain tumbling, where chains continually collapse and elongate as their associations break and reform within the advecting network. This produces a broad, nearly uniform distribution of chain stretch over a wide range of strain rates, manifesting as a rate-independent plateau in the extensional stress. Our results show that the nonlinear viscoelasticity of associative networks is dominated by large fluctuations in molecular response, which cannot be captured by current mean-field models.

DOI: [10.1103/kgrd-8gkb](https://doi.org/10.1103/kgrd-8gkb)

Associative polymer networks (APNs) are self-assembled networks that form when polymer chains interconnect through a variety of transient and reconfigurable chemical bonds [1,2]. Unlike conventional thermosets, APNs can constantly rearrange their network topology and can adapt in response to stimuli like flow or environmental conditions [3,4]. Bugs and insects routinely exploit this adaptivity to produce associative silk fibers and webbing, and many researchers wish to replicate these biological materials to create novel and sustainable polymers [4–7]. Extraordinarily, the linear viscoelasticity of APNs shows broad chemical universality, such that the linear response of many different associative chemistries can be captured by the same renormalized tube models [8–10]. However, this simple picture does not extend to highly nonlinear flows where APNs display novel physics and flow behavior that are difficult to predict and control [11].

Filament stretching experiments of various APN chemistries have shown that they display substantial strain hardening relative to unassociative melts [12–17]. This enhanced strain hardening implies that associative bonds slow chain relaxation and thus enhance chain stretching, which is consistent with mean-field ideas for linear response. However, experiments have also observed APNs to display a dramatic rate thinning of the extensional

viscosity η_E [12] with systems of varying association density all displaying near-perfect rate thinning, $\eta_E \sim \dot{\epsilon}^{-1}$, indicative of an emergent rate-independent plateau stress σ_E^* . Some new physics drives the emergence of this stress scale, which is not anticipated by current models or observed in unassociative melts that usually display a thinning exponent of $-1/2$ [18,19].

Schaefer and McLeish recently proposed that the physics governing APN viscoelasticity could be large fluctuations in chain stretch during flow [20]. Their theory predicts that flow drives convective rearrangement of associative bonds, causing chains to develop broad distributions of chain stretch such that a small fraction of highly stretched chains can dominate the nonlinear rheology—in violation of mean-field approximations. In later studies, Schaefer and McLeish argue that it is precisely these stretch fluctuations that enable silkworms to spin highly crystalline silk fibers in ambient conditions [21,22]. If true, then understanding the physics of associative stretch fluctuations could be the key to discovering better bioinspired methods for processing sustainable polymers.

Here, we apply nonequilibrium molecular dynamics simulations of coarse-grained APNs [23] to characterize the coupling between bond dynamics and nonlinear extensional flows. Our simulations reproduce the macroscopic strain hardening and rate thinning of η_E observed in experiments on H-bonding polyacrylates [12], and directly relate these trends to large fluctuations in chain stretch that are consistent with the theoretical predictions of Schaefer and McLeish. We observe that both features are mediated by a new form of nonequilibrium chain dynamics in which associative chains tumble between collapsed and highly

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

extended states during extensional flow. This “extensional tumbling” is driven by dynamic fluctuations in tension along chain backbones as associative bonds are driven to break and reform in the advecting network. This is reminiscent of the tumbling observed for entangled chains in shear flow [24], but it arises in the absence of bulk vorticity.

We simulate linear melts of $M = 2000$ chains of length $N = 80$ monomers using a semiflexible Kremer-Grest bead-spring model [25]. Monomers interact via a purely repulsive Lennard-Jones (LJ) potential truncated at a cutoff $r_c = 2^{1/6}\sigma_{\text{LJ}}$. All physical quantities are reported in reduced LJ units of length σ_{LJ} , energy ϵ_{LJ} , and time $\tau_{\text{LJ}} = \sqrt{m\sigma_{\text{LJ}}^2/\epsilon_{\text{LJ}}}$. Monomers are connected into chains by finitely extensible nonlinear elastic potential bonds with an average bond length $b \approx 0.96\sigma_{\text{LJ}}$ [25]. The stiffness of chain backbones is set by applying a bending potential $k_\theta(1 - \cos \theta)$ between adjacent bonds, where θ is the angle between each pair and $k_\theta = 1.5\epsilon_{\text{LJ}}$. Melts were prepared and equilibrated at monomer number density $\rho = 0.85\sigma_{\text{LJ}}^{-3}$ and temperature $T = 1.0\epsilon_{\text{LJ}}/k_B$, following the same way in our prior study [23]. These conditions produce model melts with an entanglement segment length $N_e \approx 28$ beads [26], an entanglement relaxation time $\tau_e \approx 1980\tau_{\text{LJ}}$ [26–28], and a bare Rouse time $\tau_R^0 = \tau_e(N/N_e)^2 \approx 16163\tau_{\text{LJ}}$. All simulations were performed using LAMMPS [29].

Our associative melts are made by replacing four normal monomers on each chain with bivalent associative monomers that interact via a three-body Tersoff potential detailed in our recent paper [23]. We evenly space associative monomers along chain backbones by replacing the tenth bead in every 20-bead subsegment with an associative bead. Our associative potential has two key parameters: the cohesive strength of an associative dimer $U/k_B T$ and an energy barrier $E_x/k_B T$ for forming an associative trimer [23]. Varying these two parameters can realize the kinetics of a variety of associative chemistries, including H-bonding networks and covalent adaptive networks. Here, we model systems with $U/k_B T = 9, 12, 15$, or 18 , and $E_x/k_B T = 0.5U/k_B T$, which display dissociative-type kinetics akin to H-bonding networks. Following our prior study, we measure the equilibrium associative bond relaxation time, i.e., the “sticky” relaxation time or sticker lifetime τ_s^{eq} , for each system to be $\tau_s^{\text{eq}} \approx \sim 7.1 \times 10^3, 9.7 \times 10^4, 1.1 \times 10^6$, and $1.02 \times 10^7 \tau_{\text{LJ}}$. Our unassociative melt systems are labeled as KG, representing Kremer-Grest normal melts.

Equilibrated melts are deformed in uniaxial extensional flow at a constant Hencky strain rate $\dot{\epsilon} = \dot{L}/L$ with L the length of the system along the elongating z -axis. The transverse dimensions contract to maintain a constant volume. Flow is simulated using generalized Kraynik-Reinelt boundary conditions [30,31] and by integrating the g-SLLOD equations of motion [32,33]. The transient extensional stress $\sigma_E(t) = \sigma_{zz} - \frac{1}{2}(\sigma_{xx} + \sigma_{yy})$ is computed

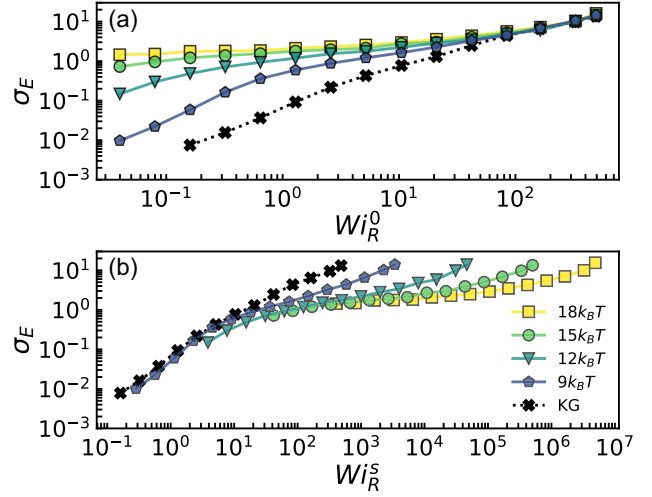


FIG. 1. Steady extensional stress of unassociative KG and associative melts with different cohesive strength of stickers under varying strain rates relative to (a) the original Rouse time τ_R^0 for all systems, and (b) the sticky-Rouse time τ_R^s for associative systems and τ_R^0 for unassociative melts.

during flow, and steady-state statistics are calculated by averaging simulation data over the strain interval $\epsilon \in [4, 10]$. Strain rates are reported in terms of two dimensionless Weissenberg numbers $Wi_R^0 = \dot{\epsilon}\tau_R^0$ and $Wi_R^s = \dot{\epsilon}\tau_R^s$, normalized by either the intrinsic Rouse time of the melt with no associative bonds τ_R^0 or a system-specific sticky-Rouse time $\tau_R^s = \tau_s^{\text{eq}} f^2$, where $f = 4$ is the number of stickers per chain and τ_s^{eq} is the sticker association lifetime measured for each system in equilibrium.

Figure 1 shows the steady-state extensional stress σ_E versus strain rate for dissociative-type associative and unassociative systems. As shown, the stresses for associative systems are significantly higher than those for the unassociative melt at low rates $Wi_R^0 < 1$, but they converge onto a common curve once $Wi_R^0 \sim 40$. This convergence corresponds to stretched chain backbones approaching their maximum extension, as shown in Fig. S1(a) [34]. In this limit, the finite extensibility of the chain backbone dominates over the chemical interactions between chains in the dissipative stress.

The rate dependence of σ_E is controlled by the cooperative relaxation dynamics of associative bonds, which becomes clear when the stress data are replotted in Fig. 1(b) with rates normalized by the sticky-Rouse time τ_R^s of each system. For the unassociative case (black X), $\tau_R^s = \tau_R^0$. With this normalization, all systems collapse onto a common low-rate envelope that displays an initial power-law rise toward a common stress plateau once $Wi_R^s \sim 1$. Each system remains in this stress plateau until finite extensibility overtakes the dynamics at high rates. The common response of systems below $Wi_R^s \sim 1$ is consistent with the

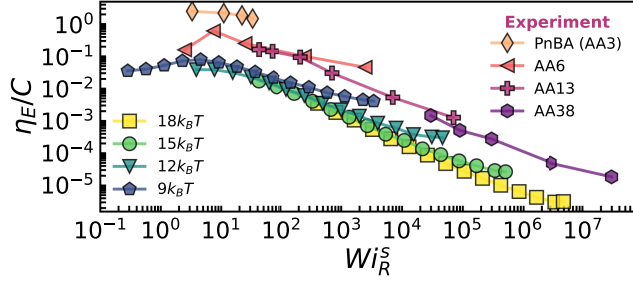


FIG. 2. Comparison on normalized extensional viscosity of associative melts with varying bond strengths and experiment [12] on poly(n-butyl acrylate) (PnBA) and PnBA-poly(acrylic acid) H-bonding copolymers with varying percentages of acrylic acid (AA) associative groups. Viscosities are scaled vertically by a constant C for visual comparison, where $C = \tau_R^s$ and $10^4 \tau_R^s$ for simulations and experiments, respectively.

ideas of the sticky-Rouse model, but the subsequent stress plateau is unanticipated by mean-field theories. As we will show, this plateau is also governed by the dynamics of associations that drive chains to tumble as they fluctuate in extensional flow.

MD predictions for the steady-state viscosity $\eta_E(\dot{\epsilon})$ agree well with experiments. Figure 2 plots η_E versus $Wi_R^s = \dot{\epsilon} \tau_R^s$ for both simulations and filament stretching experiments on acrylate-based H-bonding networks [12]. Experimental η_E are taken from the terminal values of the published transient viscosities, and the relaxation times of their H-bonding copolymers are taken from the fitted models of Wanger *et al.* [35]. Both simulations and experiments predict flow curves with near-perfect rate thinning, $\eta_E = \sigma_E / \dot{\epsilon} \sim \dot{\epsilon}^{-1}$, consistent with a rate-independent plateau in extensional stress like we observe. Experiments and simulations also show similar signatures of finite extensibility, with systems lifting off the master curve at the highest rates. The extent of the power-law thinning regime grows with increasing $U/k_B T$ in simulations and with increasing acrylic acid content in the experiments. In the context of our analysis, both strategies increase τ_R^s and should increase the plateau width.

To understand the molecular origin of the stress plateau, we plot the steady-state distribution of chain end-to-end vectors $P(R)$ in Fig. 3 for several Wi_R^0 . For the unassociative melt shown in Fig. 3(a), chains elongate uniformly during extension, producing a peaked distribution that moves to larger $\langle R \rangle$ with increasing strain rate. This is consistent with past studies [36,37] and produces a monotonic rise in $\sigma_E(\dot{\epsilon})$ as observed in Fig. 1. The molecular response of APN systems is very different and is shown in Fig. 3(b) for the $U/k_B T = 18$ system. Once $Wi_R^s \sim 1$, APN distributions flatten into a broad and almost uniform distribution that persists as the strain rate increases. This means that the steady-state flow is populated by chains elongated to essentially all extensions in equal measure, the extreme limit of molecular-scale fluctuations.

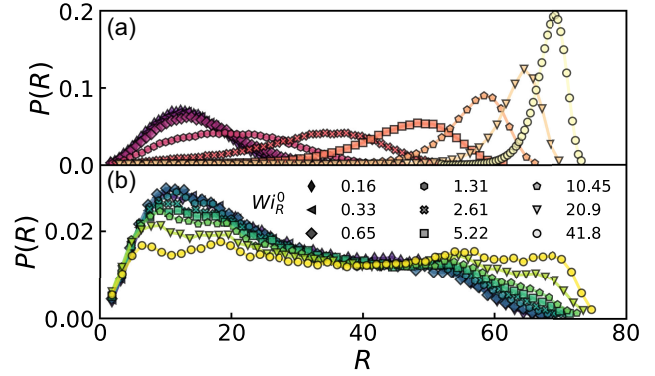


FIG. 3. Distribution function $P(R)$ of end-to-end distance R for (a) unassociative melts and (b) associative melts with $U = 18k_B T$ under uniaxial extensional flow at varying strain rates relative to the original Rouse time Wi_R^0 . The corresponding Weissenberg numbers based on the sticky-Rouse time, Wi_R^s , range from 1.6×10^3 to 4.2×10^5 .

The extensional stress σ_E is often modeled as a function of the *average* chain elongation $\langle R \rangle$, and it is common to use such models to infer molecular structure from rheological data. This correspondence works well for normal melts, since $P(R)$ is peaked and its average captures the state of most chains. However, for associative networks, the broad $P(R)$ results in a *smaller* average chain stretch $\langle R \rangle$, which is expected to correspond to lower macroscopic stress compared to normal melts. This expectation from mean-field theory is completely contradicted by the stresses shown in Fig. 1(a). Hence, the stress is not particularly meaningful for interpreting the behavior of the chains, since the average $\langle R \rangle$ is not representative of the majority of the fluid. Additionally, such low average chain stretches counterintuitively correspond to a highly oriented average chain alignment with the flow direction, as shown in Fig. S1(c) [34].

One might ask if the wide stretch distributions in Fig. 3(b) are due to associations trapping some chains in particularly strong associative clusters, but we observe this is not the case. Instead, all chains respond uniformly to flow, but their response is characterized by large fluctuations, with chains continuously tumbling between unstretched and highly stretched states during steady flow. Fluctuating chain trajectories for $R(t)$ are shown in Fig. 4(a) for the strongest $U = 18k_B T$ system at $Wi_R^0 \approx 42$. We term this behavior *extensional tumbling*, since it resembles the end-over-end reorientation that entangled chains display in simple shear flows [24,38]. However, while chain tumbling in shear is driven by flow vorticity, this “extensional tumbling” is driven by stochastic fluctuations in intermolecular associative bonds.

The broad distribution of chain stretch accumulates as chains rapidly tumble toward sequence-specific conformations, as illustrated in Fig. 4(b). Chains approach particular conformations based on the specific engagement of their

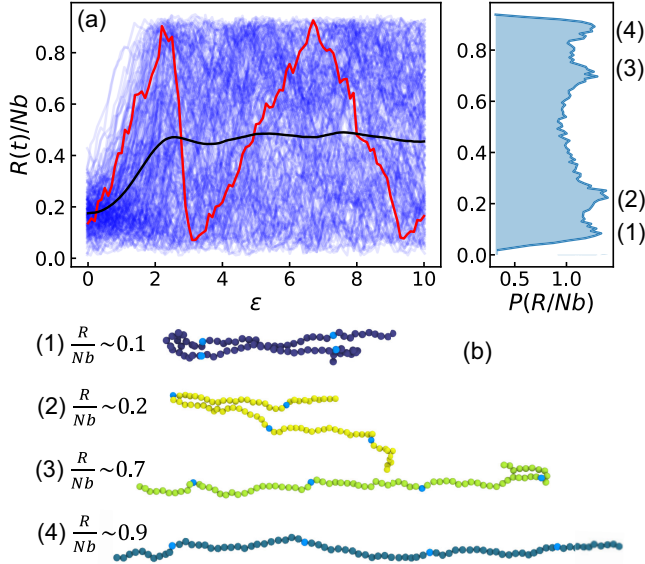


FIG. 4. (a) End-to-end extension ratios R/Nb versus strain of chains with $U/k_B T = 18$ and $Wi_R^0 = 41.8$. Blue lines are single chain trajectories. The solid black line is the average trajectory. The red line highlights one chain to show its fluctuations over time. The right panel shows the average distribution $P(R/Nb)$ in steady state. (b) Depictions of individual chain conformation associated with numbered peaks in $P(R/Nb)$, with stickers highlighted in light blue.

associative bonds and the relative velocities of the segments they are connected to. As associative bonds dissociate or exchange, chains experience large fluctuations in tension that drive them to rapidly reconfigure toward new conformations. This constant cycling between extended and collapsed states produces a broad distribution of $P(R)$. For sufficiently large $U/k_B T$, as in Figs. 3 and 4, sequence-specific conformations can manifest peaked features in the stretch distribution $P(R)$.

The sticky-Rouse model predicts associative bonds slow chain relaxation and enhance chain stretch with increasing $U/k_B T$. However, tumbling chains show the opposite trend, with $\langle R \rangle$ decreasing at fixed Wi_R^0 as $U/k_B T$ increases (see Fig. S1 [34]). This is because both the stretch and collapse of tumbling chains are driven by the same fluctuations in tension. Fluctuating bond configurations drag chains into collapsed and stretched conformations alike. This gives more uniform $P(R)$ as Wi_R increases.

The timescale for tumbling can be quantified by following the approach of Sefiddashti *et al.* for linear chains in shear [24]. We extract a convective tumbling time τ_c by measuring the decay of the time-autocorrelation function of the unit end-to-end vector $\vec{u}$, averaged over all chains in steady state: $f(t) = \langle \vec{u}(t) \cdot \vec{u}(t + \tau) \rangle$. We observe $f(t)$ displays a simple exponential decay e^{-t/τ_c} from which we extract τ_c [see Fig. S2(a) [34]]. Notably, the pure exponential decay in $f(t)$ differs from the form observed

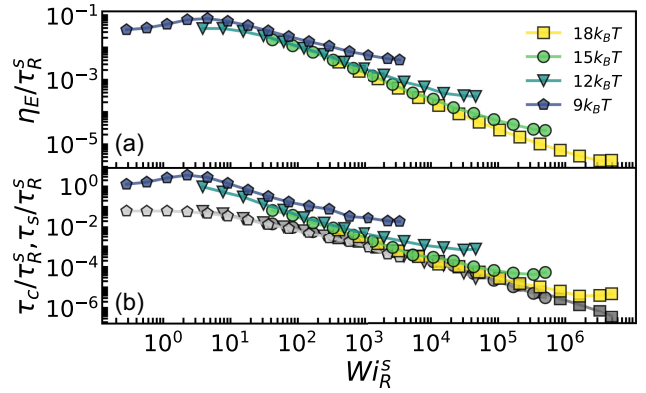


FIG. 5. (a) Scaled steady-state extensional viscosity η_E and (b) scaled tumbling timescale τ_c and sticker lifetime τ_s (in gray) for associating networks with different cohesive energy of stickers. η_E , τ_c , and τ_s are all normalized by sticky-Rouse timescale τ_R^s .

for unassociative chains tumbling in shear, which show a decaying oscillation $f \sim \sin(\omega t)e^{-t/\tau}$ where ω and τ^{-1} are comparable in magnitude. This is due to the fact that APN tumbling is mediated by rapid reorientation events that occur abruptly as chemical associations break and reform.

Figure 5(b) plots the normalized tumbling time τ_c/τ_R^s versus Wi_R^s for all four $U/k_B T$. Normalizing by τ_R^s collapses the data onto a common curve that displays a nonmonotonic shape and strongly resembles that of the viscosity η_E , replotted in Fig. 5(a). At low $Wi_R^s < 1$, the tumbling time approaches the sticky-Rouse time $\tau_c \sim \tau_R^s$ as chain reorientation is described by the sticky-Rouse model near equilibrium. For large $Wi_R^s \gg 1$, the tumbling time follows a power law as it approaches the sticky relaxation time of individual associations τ_s , plotted as gray symbols in Fig. 5(b). In this limit, chain tumbling is limited by the speed at which individual associations reform. At intermediate $Wi_R^s \sim 1$, τ_c reaches a maximum, indicating a slowdown in the tumbling process as chains begin to elongate. These trends in τ_c mirror trends in the fraction of intramolecular associations (see Fig. S3 [34]).

Previous studies [39–44] have generally agreed that the nonequilibrium kinetics of bond dissociation should govern the rate dependence of the APN viscosity, but the cooperative mechanisms mediating this relationship have not been established. Figure 5 shows that the viscosity $\eta_E \sim \tau_c$, with both displaying a common shape, including a maximum at $Wi_R^s \sim 1$. But this maximum is notably absent in the rate dependence of τ_s . This strongly suggests that the timescale for nonlinear dissipation is governed by chain tumbling and the nonmonotonic viscosity emerges from the cooperative interaction of separate chains within the network, rather than from the kinetics of individual associative bonds.

The tumbling we observe here can be thought of as a nonequilibrium generalization of chain “brachiation”

described by Cai and Spakowitz, where an associative chain “swings” its segments through the network, similar to how a monkey swings from branch to branch through a forest [45]. Our prior simulations of the same model APNs measured chain brachiation times in equilibrium and showed that this timescale governs the terminal relaxation time of binary APNs [23]. The present Letter now reveals that nonlinear flows drive brachiating chains to undergo dramatic fluctuations in chain stretch as chain segments swing between sections of the network that are advecting in different directions.

Notably, the extensional tumbling we observe in APNs is not observed in other transient polymer networks mediated by topological entanglements [36] or uncoordinated ionic aggregates [46], despite all displaying similar sticky-Rouse or reptation linear viscoelasticity. Instead, it seems that different forms of intermolecular constraints can drive different nonequilibrium mechanisms coupling network relaxation to flow [46–48]. Thus, while many APN chemistries display universal functional form in linear response, the precise nature, coordination, and kinetics of associative complexes appear to drive fundamentally different nonlinear dynamics.

To conclude, we have shown that a chemically generic coarse-grained model for bivalent APNs accurately predicts the experimental power-law rate thinning of the extensional viscosity of H-bonding networks [12]. Simulations relate the strong power-law thinning of η_E to a rate-independent plateau in both stress and average chain elongation, which develops as associative bond fluctuations drive chains to undergo a novel form of tumbling in extensional flow. The fluctuating associations connecting a chain to the flowing network produce local tension imbalances along chain backbones, driving chains to continuously elongate and collapse. Tumbling chains develop a broad distribution of chain stretch with a rate-insensitive average that persists until chains approach the finite extensibility limit, where viscous drag dominates. This process is consistent with the theoretical arguments made by Schaefer and McLeish for associative silks [20–22].

Despite its minimal description of associative interactions, our model shows good agreement with experiments. This suggests that the extensional tumbling we observe may be a generic feature of APNs with binary coordination. We suspect that other association coordinations and kinetics may give rise to even more novel behaviors and flow sensitivities. Our future work aims to explore how varying these parameters influences APN dynamics and rheology. We believe that our coarse-grained models will be a valuable tool for understanding the physics of this complex chemical landscape.

Acknowledgments—This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DESC0025643. This

work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE’s National Nuclear Security Administration under Contract No. DE-NA-0003525.

The views expressed in this article do not necessarily represent the views of the U.S. DOE or the U.S. Government.

Data availability—The data that support the findings of this Letter are openly available [49]; embargo periods may apply.

-
- [1] S. Wu and Q. Chen, Advances and new opportunities in the rheology of physically and chemically reversible polymers, *Macromolecules* **55**, 697 (2022).
 - [2] Z. Zhang, Q. Chen, and R. H. Colby, Dynamics of associative polymers, *Soft Matter* **14**, 2961 (2018).
 - [3] W. H. Binder and R. Zirbs, Supramolecular polymers and networks with hydrogen bonds in the main- and side-chain, *Adv. Polym. Sci.* **207**, 1 (2006).
 - [4] A. M. Wemyss, C. Ellingford, Y. Morishita, C. Bowen, and C. Wan, Dynamic polymer networks: A new avenue towards sustainable and advanced soft machines, *Angew. Chem., Int. Ed. Engl.* **60**, 13725 (2021).
 - [5] M. J. Webber and M. W. Tibbitt, Dynamic and reconfigurable materials from reversible network interactions, *Nat. Rev. Mater.* **7**, 541 (2022).
 - [6] C. Guo, C. Li, X. Mu, and D. L. Kaplan, Engineering silk materials: From natural spinning to artificial processing, *Appl. Phys. Rev.* **7**, 011313 (2020).
 - [7] V. Volkov, A. V. Ferreira, and A. Cavaco-Paulo, On the routines of wild-type silk fibroin processing toward silk-inspired materials: A review, *Macromol. Mater. Eng.* **300**, 1199 (2015).
 - [8] L. G. Baxandall, Dynamics of reversibly cross-linked chains, *Macromolecules* **22**, 1982 (1989).
 - [9] L. Leibler, M. Rubinstein, and R. H. Colby, Dynamics of reversible networks, *Macromolecules* **24**, 4701 (1991).
 - [10] M. Rubinstein and A. N. Semenov, Dynamics of entangled solutions of associating polymers, *Macromolecules* **34**, 1058 (2001).
 - [11] I. Mahmad Rasid, J. Ramirez, B. D. Olsen, and N. Holten-Andersen, Understanding the molecular origin of shear thinning in associative polymers through quantification of bond dissociation under shear, *Phys. Rev. Mater.* **4**, 055602 (2020).
 - [12] A. Shabbir, H. Goldansaz, O. Hassager, E. Van Ruymbeke, and N. J. Alvarez, Effect of hydrogen bonding on linear and nonlinear rheology of entangled polymer melts, *Macromolecules* **48**, 5988 (2015).

- [13] C. R. López-Barrón, J. Lu, J. A. Throckmorton, H. Passino, and M. Gopinadhan, Microstructure, viscoelasticity, and extensional rheology of ethylene-propylene copolymer vitrimers, *Macromolecules* **57**, 2729 (2024).
- [14] C. R. López-Barrón, J. A. Throckmorton, and T.-P. Lin, Extensional rheology and flow-induced crystal alignment in polypropylene ionomers, *J. Rheol.* **66**, 657 (2022).
- [15] S. Wu, X. Cao, Z. Zhang, Q. Chen, Y. Matsumiya, and H. Watanabe, Molecular design of highly stretchable ionomers, *Macromolecules* **51**, 4735 (2018).
- [16] A. Shabbir, Q. Huang, G. P. Baeza, D. Vlassopoulos, Q. Chen, R. H. Colby, N. J. Alvarez, and O. Hassager, Non-linear shear and uniaxial extensional rheology of polyether-ester-sulfonate copolymer ionomer melts, *J. Rheol.* **61**, 1279 (2017).
- [17] G. H. Ling, Y. Wang, and R. A. Weiss, Linear viscoelastic and uniaxial extensional rheology of alkali metal neutralized sulfonated oligostyrene ionomer melts, *Macromolecules* **45**, 481 (2012).
- [18] Q. Huang, When polymer chains are highly aligned: A perspective on extensional rheology, *Macromolecules* **55**, 715 (2022).
- [19] S. Costanzo, Q. Huang, G. Ianniruberto, G. Marrucci, O. Hassager, and D. Vlassopoulos, Shear and extensional rheology of polystyrene melts and solutions with the same number of entanglements, *Macromolecules* **49**, 3925 (2016).
- [20] C. Schaefer and T. C. McLeish, Power law stretching of associating polymers in steady-state extensional flow, *Phys. Rev. Lett.* **126**, 057801 (2021).
- [21] C. Schaefer, P. R. Laity, C. Holland, and T. C. McLeish, Stretching of Bombyx mori silk protein in flow, *Molecules* **26**, 1 (2021).
- [22] C. Schaefer and T. C. B. McLeish, Theoretical rheo-physics of silk: Intermolecular associations reduce the critical specific work for flow-induced crystallization, *J. Rheol.* **66**, 515 (2022).
- [23] S. Liu and T. C. O'Connor, A reactive bead-spring model for associative polymer melts in and out of equilibrium, *Macromolecules* **57**, 1403 (2024).
- [24] M. H. Nafar Sefiddashti, B. J. Edwards, and B. Khomami, Individual chain dynamics of a polyethylene melt undergoing steady shear flow, *J. Rheol.* **59**, 119 (2015).
- [25] K. Kremer and G. S. Grest, Dynamics of entangled linear polymer melts: A molecular-dynamics simulation, *J. Chem. Phys.* **92**, 5057 (1990).
- [26] L. A. Moreira, G. Zhang, F. Müller, T. Stuehn, and K. Kremer, Direct equilibration and characterization of polymer melts for computer simulations, *Macromol. Theory Simul.* **24**, 419 (2015).
- [27] H. P. Hsu and K. Kremer, Static and dynamic properties of large polymer melts in equilibrium, *J. Chem. Phys.* **144** (2016).
- [28] T. Ge, M. O. Robbins, D. Perahia, and G. S. Grest, Healing of polymer interfaces: Interfacial dynamics, entanglements, and strength, *Phys. Rev. E* **90**, 012602 (2014).
- [29] A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton, LAMMPS—A flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales, *Comput. Phys. Commun.* **271**, 108171 (2022).
- [30] M. Dobson, Periodic boundary conditions for long-time nonequilibrium molecular dynamics simulations of incompressible flows, *J. Chem. Phys.* **141**, 184103 (2014).
- [31] D. A. Nicholson and G. C. Rutledge, Molecular simulation of flow-enhanced nucleation in n-eicosane melts under steady shear and uniaxial extension, *J. Chem. Phys.* **145**, 244903 (2016).
- [32] D. J. Evans and G. P. Morriss, Nonlinear-response theory for steady planar Couette flow, *Phys. Rev. A* **30**, 1528 (1984).
- [33] P. J. Daivis and B. D. Todd, A simple, direct derivation and proof of the validity of the SLLOD equations of motion for generalized homogeneous flows, *J. Chem. Phys.* **124**, 194103 (2006).
- [34] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/kgnd-8gkb> for additional figures plotting steady-state statistics for chain conformations, chain tumbling, and the time evolution of network connections during startup flow.
- [35] M. H. Wagner, E. Narimissa, and A. Shabbir, Modelling the effect of hydrogen bonding on elongational flow of supramolecular polymer melts, *Rheol. Acta* **61**, 637 (2022).
- [36] T. C. O'Connor, N. J. Alvarez, and M. O. Robbins, Relating chain conformations to extensional stress in entangled polymer melts, *Phys. Rev. Lett.* **121**, 047801 (2018).
- [37] T. C. O'Connor, A. Hopkins, and M. O. Robbins, Stress relaxation in highly oriented melts of entangled polymers, *Macromolecules* **52**, 8540 (2019).
- [38] C. M. Schroeder, R. E. Teixeira, E. S. Shaqfeh, and S. Chu, Characteristic periodic motion of polymers in shear flow, *Phys. Rev. Lett.* **95**, 018301 (2005).
- [39] A. Vaccaro and G. Marrucci, A model for the nonlinear rheology of associating polymers, *J. Non-Newtonian Fluid Mech.* **92**, 261 (2000).
- [40] F. Tanaka, Viscoelastic properties of physically crosslinked networks part 2. Dynamic mechanical moduli, *J. Non-Newtonian Fluid Mech.* **43**, 273 (1992).
- [41] F. Tanaka and S. F. Edwards, Viscoelastic properties of physically cross-linked networks. Transient network theory, *Macromolecules* **25**, 1516 (1992).
- [42] F. Tanaka and S. F. Edwards, Viscoelastic properties of physically crosslinked networks part 3. Time-dependent phenomena, *J. Non-Newtonian Fluid Mech.* **43**, 289 (1992).
- [43] F. Tanaka and S. F. Edwards, Viscoelastic properties of physically crosslinked networks part 1. Non-linear stationary viscoelasticity, *J. Non-Newtonian Fluid Mech.* **43**, 247 (1992).
- [44] M. K. Sing, Z. G. Wang, G. H. McKinley, and B. D. Olsen, Celebrating soft matter's 10th anniversary: Chain configuration and rate-dependent mechanical properties in transient networks, *Soft Matter* **11**, 2085 (2015).
- [45] P. C. Cai, B. A. Krajina, and A. J. Spakowitz, Brachiation of a polymer chain in the presence of a dynamic network, *Phys. Rev. E* **102**, 020501(R) (2020).
- [46] S. S. Mohottalage, M. Senanayake, J. T. Clemmer, D. Perahia, G. S. Grest, and T. O'Connor, Nonlinear elongation flows in associating polymer melts: From homogeneous to heterogeneous flow, *Phys. Rev. X* **12**, 021024 (2022).

- [47] R. S. Graham, A. E. Likhtman, T. C. B. McLeish, and S. T. Milner, Microscopic theory of linear, entangled polymer chains under rapid deformation including chain stretch and convective constraint release, *J. Rheol.* **47**, 1171 (2003).
- [48] S. S. Mohottalalage, A. P. Saab, and A. Maiti, Bead-spring simulation of ionomer melts—Studying the effects of chain-length and associating group fraction on equilibrium structure and extensional flow behavior, *Polymers* **15**, 4560 (2023).
- [49] L. Songyue and Thomas C. O’Connor, 2025, Simulation files and plotted data are freely available at https://github.com/OConnor-Lab/APN_Flow_Liu_PRL_2025.