

**Non-linear Rheology · linear and star
Polymers · Neutron Scatter**

The molecular-level response to shear of entangled polymers at interfaces and in the bulk has been of interest to understand the non-linear rheological response of polymers. Here we focus on the molecular level response to shear strain leading non-linear rheological phenomenon, in linear and star polymers comparing the observed response to the predictions of tube theory. We used SANS measurements of the bulk polymer response to shear in Couette geometry on melts of high molecular weight mixtures of polymers extending our previous results on interfacial responses with rheoNR measurements in cone-and-plate geometry.[1, 2] further development of the theory.

**Molekulare Polymerschmelzen
die auf Scherung in linearen und
nicht linearen rheologischen Be-
reichen reagieren: Auswirkungen
von Molekulargewicht und
komplexer Architektur****Nicht lineare Rheologie · lineare und
sternförmige Polymere · Neutronen-
streuung**

Die Veränderungen von verschlauften Polymeren in Schmelze und an Grenzflächen auf molekularer Ebene unter Scherung sind für das Verständnis der nichtlinearen rheologischen Eigenschaften von Interesse. Die vorgestellten Untersuchungen von linearen und sternförmigen Polymeren konzentrieren sich auf die molekularen Auswirkungen von Scherbelastung im Bereich der nichtlinearen Rheologie. Vorhersagen des Röhrenmodells werden mit den experimentellen Ergebnissen verglichen. Sans Untersuchungen unter Scherung an Polymerschmelzen mit höheren Molekulargewichten und Mischungen in einer Couette Geometrie ergänzen existierende Ergebnisse zu Grenzflächeneigenschaften gemessen mittels rheoNR in einer Kegel-Platte-Anordnung. [1, 2]

Figures and Tables: By a kind approval of the authors.

Molecular-Scale Polymer Melts Response to shear in the linear and non-linear rheological Domains: Affect of molecular Weight and complex Architecture

Background and Scientific Importance

The problem of understanding the relationship between the bulk rheological properties of entangled polymeric liquids and the polymer molecular architecture is one of the most interesting and important problems of polymer science.[3, 4] Polymers, as non-Newtonian fluids, exhibit a number of critical rheological properties from a practical and industrial perspective,[5-9] as under high strain rates, $\dot{\gamma}$ (Hz), polymers show non-linear viscoelastic properties, the structural fundamentals of which are not well understood. Furthermore, there is interest in mixtures of linear polymers with those having complex architectures, such as stars, for producing blends with optimal properties.[10, 11]

The theoretical framework of the relationships among rheological behavior and the molecular structural responses of entangled polymers is based largely on tube models, in which a mean field tube, formed by a polymer chain's neighbors, represents the conformational constraints on the chain from entanglements with its neighbors. The tube restricts the lateral but not the curvilinear chain motion. Chain rearrangements within the tube occur very fast over the Rouse entanglement segment relaxation time, τ_e . Movement over the entire chain length, the Rouse time, in the tube is considerably longer, as $\tau_R = Z^2\tau_e$, where Z is the number of entanglements. The chain must escape the tube in order to relax stress. There is a hierarchy of ways that the polymer deforms and then relaxes toward equilibrium, due to topological constraints imposed by the tube and its motion relative to the test polymer. There are multiple first order relaxation processes involved, in which the polymer and confining tube move relative to each other. These occur over time scales, $\tau_i \sim \dot{\gamma}^{-1}$ over several orders of magnitude,[3, 4, 12, 13] and they are included in the fundamen-

tal theory of de Gennes, Doi and Edwards.[14-20] The slowest of these is reptation, $\tau_d = 3Z^3\tau_e$, which is the time required for a linear chain to escape the tube. This mechanism cannot occur with a star polymer due to the constraints imposed on an arm by the other arms. [21] The others in decreasing characteristic times, thus active at increasing $\dot{\gamma}$, are contour length fluctuation (CLF), convective constraint release (CCR) and constraint Rouse relaxation (CRR). CLF allows that the end of the test chain can retract from the confining tube then extend into a new tube region. In the linear rheological regime, with a linear polymer, reptation and CLF relaxation processes result from chain diffusion. This problem is more complex in the nonlinear regime, where the test chains must move relative to the confining tube as a consequence of the viscous flow. This results in an alteration of the chain entanglements and the confining tube geometry. The forced perturbations on the polymer chain conformation requires CCR.[22-24] In CCR the perturbation time scale is much faster than the time scale of the tube to reform. Polymer stretching, CRR, is predicted over higher $\dot{\gamma}$, as, $\tau_r \gg \dot{\gamma}^{-1}$. [3, 4] By including these mechanisms McLeish and colleagues[11, 25-28] have develo-

Authors:

Rex P. Hjelm, Leslie A Sasa, Erik J. Yearley,
Luke T. Andriano, Nino Roucco,
Daniel P. Olds, L. Gary Leal,
Los Alamos, NM 87544 USA

Corresponding Author:
Rex P. Hjelm
New Mexico Consortium
4200 W Jemez Rd #200, Los Alamos,
NM 87544 USA
E-Mail: rexhjelm@mac.com

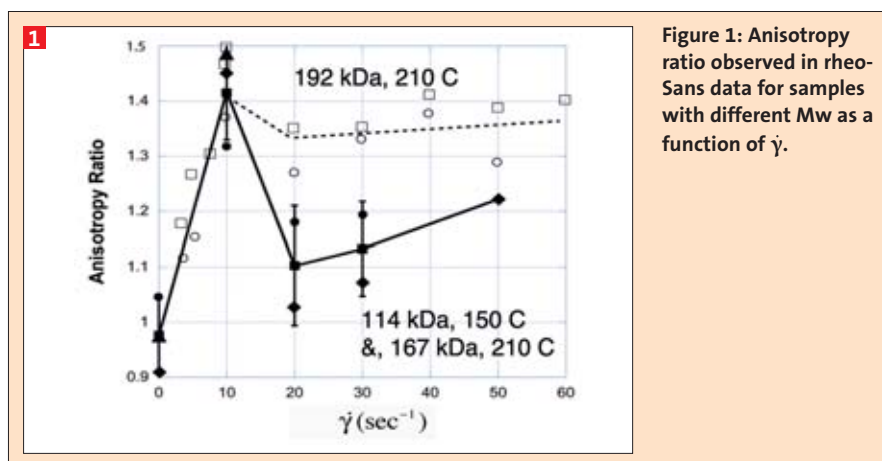


Figure 1: Anisotropy ratio observed in rheo-Sans data for samples with different M_w as a function of $\dot{\gamma}$.

ped the Glamm model[25] based on coherent tube theory that can be tested using appropriate measurements in the linear and non-linear rheological domains.

Tests of these theories in melts have often involved comparison between macroscopic behavior, as measured in conventional rheological tests and predictions at this same macroscopic level. The source of potential failures in the theory cannot generally be pinpointed by such comparisons.[29] Consequently, there has been extensive work to obtain direct evidence on the interaction of polymer architecture, structural response and resulting non-linear rheology in melts using rheo-optical techniques,[30, 31] neutron spin-echo scattering,[32] dielectric relaxation,[33] and Sans.[10, 12, 34-42] Regardless there is still a lack of information on these interrelationships under steady flow at high strain rates well into the non-linear regime and with polymers with complex architectures, all of which are important in polymer physics, industrial processing and reinforced durable rubber products. [5-11]

Objective and approach

We address the problem of understanding the relationship between the bulk rheological properties of entangled polymeric fluids and molecular architecture in a flow field over the non-linear rheological domain, defined by the criterion that the Weissenberg number, $Wi = \dot{\gamma}\tau_d > 1$. Previously, we considered the source of the non-linear rheological property characteristic of the CCR domain, shear thinning, where the viscosity of the melt decreases as $\eta \sim \dot{\gamma}^{-1}$. [1, 2] We looked at three plausible theories to explain the role of shear thinning as a result of interactions of surface bound polymers with the bulk:

slip-shear, or wall-slip,[43-46] exchanges of surface polymer with the bulk,[47] or disentanglement of surface-bound polymer from the bulk,[45] using rheo-NR[48] depth profiles to determine the structural response of surface-bound protonated polystyrene (h-PS) against a perdeuterated (d-PS) melt. While the tethered polymer reversibly retracted 15–20 % in the CCR domain, it remained entangled with the bulk polymer. This result was confirmed in a subsequent study.[49] Thus, the mechanism for shear thinning is likely to be from the polymer response to stress in the bulk.

As a consequence of this finding we addressed the behavior in the bulk through measurements of polymer structural responses to shear in viscous flow in Couette geometry using, rheo-SANS[50] in high molecular weight linear polymer melts[2] and in a star polymer-linear polymer melt[51] to provide critical tests of tube theory in the CCR domain for linear polymers and polymer mixtures with more complex architecture. The melts contained per-deuterated and protonated polymers. The behavior of the melt under continuous shear stress was observed by the rheo-Sans measurement. The difference in neutron scatter from the h-polymer versus d-polymer highlighted the former, such that we observed the conformation response of the entangled polymers. The response of the polymer to $\dot{\gamma}$ was measured simultaneously with the rheometric characterization of the melts.[50, 51]

Experimental

Simultaneous neutron scattering and rheological characterization used the Los Alamos Neutron Science Center neutron rheometer in Couette geometry for rheo-SANS.[50] and the Los Alamos Neutron

Science Center Sans instrument, LQD.[52, 53] Additional Sans measurements were done using CP-Sans at Oak Ridge National Laboratory. The Couette cell was designed to meet the optical requirements of the Sans measurements and to mitigate surface slip effects[54, 55] and curvilinear instabilities in elastic flow.[56-58]

Data from LQD was corrected and reduced using standard procedures for time-of-flight encoding [59, 60] and was placed in absolute units, $\frac{d\Sigma(Q)}{d\Omega}$ (cm^{-1}), of differential cross-section per unit volume. Here Q is the modulus of vector \mathbf{Q} in the scattering plane, which is defined for the case of isotropic scatter as $Q = \frac{4\pi}{\lambda} \sin\theta$, where θ is half the scattering angle, relative to the incident neutron beam with wavelength, λ . The Sans measurements were done in radial beam geometry, in which the incident neutron beam was normal to the shear-velocity plane, along the shear gradient. This geometry probed the polymer conformation along the flow plane. As shear stress leads to anisotropy in the scattering plane, vector, \mathbf{Q} is expressed as its components along, Q_x (Q_{\parallel}) and perpendicular, Q_y (Q_{\perp}) to the flow axis.

D-PS and h-PS were synthesized using anionic polymerization.[61] The PS samples for rheo-Sans reported here had molecular weights of 114, 167 and 192 kDa with polydispersity index (PI) of 1.3. The volume fraction of h-PS, ϕ , in the rheo-Sans measurements was 0.1.

The linear-star melt polymer blend consisted of a protonated polybutyldiene (h-PBD) symmetric four-arm star 176 kDa at $\phi = 0.1$ in a perdeuterated linear chain, d-PBD 89 kDa with PI of 1.08 for both the star and linear polymer, again using anionic polymerization. The star arms are roughly half the length of the linear d-PBD chain.

Results and Discussion

Linear Chain Melts

A frequency sweep measurement of the loss, $G''(\omega)$, and elastic, $G'(\omega)$, moduli of the 114 kDa sample at 150 C showed a cross over from fluid to solid like behavior between $G''(\omega)$ and $G'(\omega)$ at $\omega \cong 6\text{ s}^{-1}$, giving an estimate for the slowest characteristic relaxation time, $\tau_d \cong 0.17$ s. Using the scaling relationship that $\tau_d \cong M^{3.4}$, and applying a time-temperature shift to account for the temperature difference of the measurements, this result gives $\tau_d \cong 0.14$ s and 0.23 s for the 167 and 192 M_w samples, respectively, at 200 C. Thus, from the range of $\dot{\gamma}$, Wi spans 0.85 to 8.5 for the 114 kDa sample, 0.3 to 7 for the

167 kDa sample and 0.5 to 14 for the 192 kDa sample.

We showed in a previous presentation[2] that the 114 kDa sample in the absence of shear is modeled by the Random Phase Approximation (RPA),[62]

$$\frac{d\Sigma(Q)}{d\Omega} = (b_{h-PS} - b_{d-PS}) \frac{n}{v_m} \frac{\Phi(1-\Phi)D(R_g, Q)}{1 - 2\chi\Phi(1-\Phi)D(R_g, Q)} \quad (1)$$

where n is the average number of monomers in a single h-PS and d-PS chain and Φ is the volume fraction of one of the phases. Here, b_{d-PS} and b_{h-PS} are the scattering lengths of d-PS and h-PS monomers, v_m is the monomer excluded volume in the melt, χ is the Flory-Huggins interaction parameter between monomers of d-PS and h-PS and B is a background contribution. If the chains are in a random coil conformation (RCC), the form factor, D , is given by the Debye function,

$$D(R_g, Q) = 2 \frac{\exp(-Q^2 R_g^2) - 1 + Q^2 R_g^2}{(Q^2 R_g^2)^2} \quad (2)$$

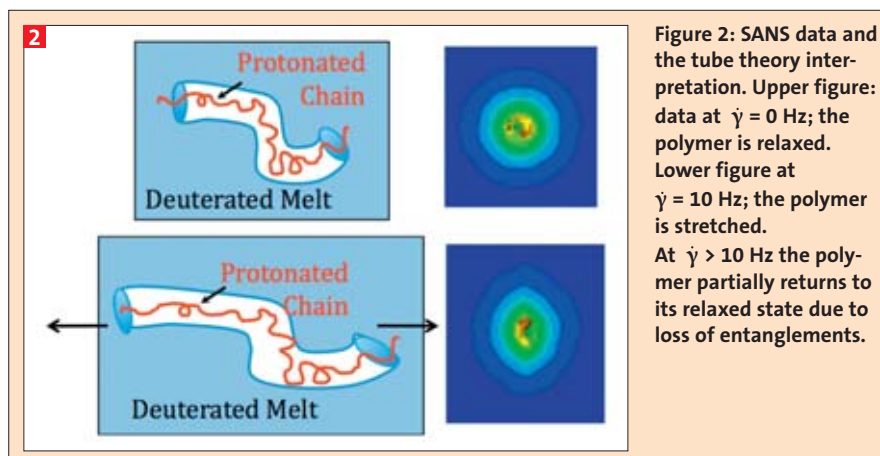
where R_g is the weight-average radius of gyration of the random coil. The same is true of the higher molecular weight, 167 and 192 kDa, polymers.

The rheo-SANS measurements “see” only the anisotropic SANS response of the protonated polymer with γ , indicative of chain alignment. Rheometry, measured simultaneously with rheo-Sans, and separate flow sweep measurements for the linear chain mixture show that stress, $\sigma = \eta\dot{\gamma}$, is constant above $\dot{\gamma} = 1$ Hz where viscosity, $\eta \sim \dot{\gamma}^{-1}$, or shear thinning is observed, as $Wi > 1$. This is characteristic of convective constraint release (CCR) of tube theory.

Linear chain anisotropy computed as,

$$A = \frac{\int_{Q_{min}}^{Q_{max}} \frac{d\Sigma}{d\Omega}(Q) dQ}{\int_{Q_{min}}^{Q_{max}} \frac{d\Sigma}{d\Omega}(Q) dQ} \quad (3)$$

(Fig. 1) is observed as $\dot{\gamma}$ increases to 10 Hz. This is illustrated schematically with examples of the two-dimensional rheo-Sans data in Figure 2. Lower molecular weight chains lose anisotropy for $\dot{\gamma} > 10$ Hz, returning to their equilibrium Gaussian chain conformation described by equations (1) and (2). Longer chains retain the anisotropy at for $\dot{\gamma} > 10$ Hz. Thus, CCR is progressive with $\dot{\gamma}$, leading to complete loss of constraint, for shorter chains, but not for longer chains, even though all mixtures showed the same $\eta \sim \dot{\gamma}^{-1}$ behavior.



Detailed analysis of the polymer response to $\dot{\gamma}$ on polymer extension with molecular weight showed that when viewed along the line of flow (Q) the polymers retain the RCC (Eq. 2) characteristic, but R_g declines roughly in proportion to the asymmetry, A (Eq.3). However, when viewed perpendicular to the line of flow (Q) the 114 kDa polymer shows power law scatter, indicative of alignment with the shear flow, with the two larger polymers being less so. These observations show alignment with flow, but with the perturbation away from the RCC due to stretching in inverse proportion to the molecular weight.

In tube theory the $\dot{\gamma}^{-1}$ dependence of the viscosity is characteristic of the CCR mechanism[23, 63-65]. The shear rates where CCR is the likely dominant mechanism for non-linear rheological response is $\tau_d \dot{\gamma} \gtrsim \tau_R$. At higher shear rates, $\tau_R \dot{\gamma} > 1$, chain stretching is predicted. This mechanism has also been invoked to explain polymer non-linear polymer rheology,[25] However, our measurements where at shear rates well below τ_R , as we estimate τ_R from Z and our estimates of τ_d , as $\tau_R = \frac{\tau_d}{3Z}$ to be 0.011, 0.006 and 0.009s for the 114, 167 and 192 kDa samples, respectively, the reciprocal of which is well above the highest shear rates used here. Thus, our measurements were within CCR domain.

Whereas the loss of constraints through the CCR mechanism should inhibit chain extension,[24] this implies that the chain extension should saturate as some value of A and level off. It has been posited[13] that chain retraction back toward the equilibrium state can occur from loss of entanglement in the CCR at sufficiently high flow rates. Estimates of the time constant for chain retraction, τ_s , gives $\tau_s =$

$2\tau_R$ [13], well above the point where we observe chain contraction. In support of the view that CCR inhibits chain orientation, Milner et al.[22] showed that CCR suppression of extension is required to explain the relatively small orientation and extension observed in the SANS measurements of PS sheared in the parallel plate geometry,[37] even at the lower shear rates used in that study.

Star-linear polymer Melt

The star polymer response at $\dot{\gamma}$ in the non-linear domain provides additional critical tests of tube theory.[51] Both the length of the star arms and the d-PDB linear matrix are entangled. However, the star while semi-dilute is below the entanglement volume fraction, estimated to be 0.15. Furthermore, the blend composition is such that the star arms do not self-entangle. Frequency sweep measurements of the loss, $G''(\omega)$, and elastic, $G'(\omega)$, moduli of the star, linear and star-linear melts at 25 °C gave cross overs from fluid to solid like behavior between $G''(\omega)$ and $G'(\omega)$ corresponding to estimates for τ_d of 16.6, 0.045 and 0.065 s, respectively. The rheo-SANS measurements were done at 25 °C, at $\dot{\gamma} = 0, 8.1, 16.1$ and 24.2 s⁻¹. Thus, the corresponding values for Wi for the rheo-Sans measurements were 0.36, 0.72 and 1.09, for the linear chain interactions. These values are largely within the linear domain of reptation and CLF relaxations, as these mechanisms for the linear polymer remain largely unchanged in the presence of a small amount of star polymers. This is consistent with a comparison of frequency sweep measurements of star and linear polymers, which show that the rheology is dominated by the linear component; thus, the rheology does not provide information on the source of the observed star rheo-Sans anisotropy.

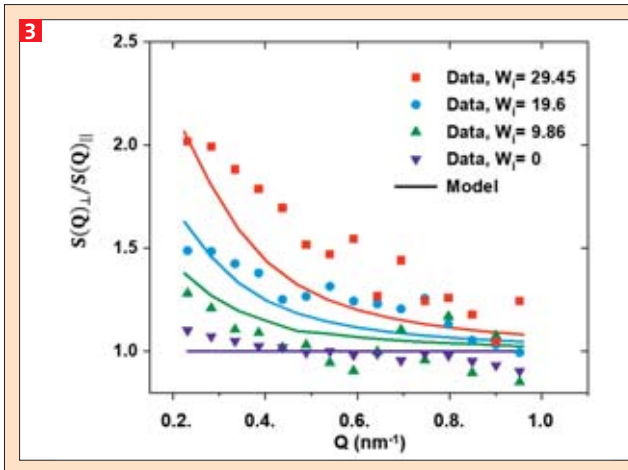


Figure 3: Anisotropy ratios for the rheoS-ANS data. Data is from ref 51.

On the other hand, the rheo-Sans signature shows that the distortion of the star arms are aligned with the flow due to entangled interactions. To obtain Wi for the star entanglements we need an estimate for the slowest relaxation time of the star arms, replacing that for reptation relaxation, which is not possible for a star, as,[51]

$$\tau' \approx \frac{2}{3\pi^2} \tau_d Z_{arm}^2, \quad (4)$$

with τ_d being the reptation relaxation time for the linear polymer and $Z_{arm} = 20$ the number of entanglements of a star arm. From Eq. 4. $\tau' \approx 1.2$ s ; Thus, Wi values are estimated to be 9.8, 19.6 and 29.4 at the respective $\dot{\gamma}$, well into the CCR domain.

Figure 3 shows the Q-dependent chain structure factor anisotropy ratios, $S(Q)_\perp/S(Q)_\parallel$, from the rheo-Sans of the star-linear chain melt at $\dot{\gamma} = 0$ Hz and at $Wi \approx 9.8, 19.6, 29.4$. The anisotropy shows that the orientation of the star polymer along the flow axis increases with Wi and increases with lower Q.

A model the conformation of the star arms with γ a tube theory model for linear polymers in the non-linear rheological domain Glamm[25] was modified for star polymers by the removal of relaxation by reptation, Glamm-R.[31] Glamm calculates the tube contour $\mathbf{R}(s,t)$, where s and t are continuous variables for distance along the tube and time. The stochastic evolution of \mathbf{R} is calculated through solutions for the tangential correlation function,

$$\left\langle \frac{\partial R_x(s,t)}{\partial s} \frac{\partial R_y(s,t)}{\partial s} \right\rangle, \quad (5)$$

the terms for which account for flow and the different relaxation mechanisms in tube theory.

Glamm-R captures extremely well the star behavior over larger Q-values. However, there are deviations of the modeled

anisotropy from the data at lower Q, at the largest Wi values.

The rheo-Sans results for the linear-linear and star-linear polymer mixtures indicate that a more detailed theory may be required.

Acknowledgement

This work benefited from the use of the Small-angle Neutron Scattering Instrument, LQD, at the Manuel Lujan, Jr. Neutron Scattering Center of the Los Alamos National Laboratory supported by the US. Department of Energy (USDOE) at Los Alamos National Laboratory operated by Los Alamos National Security LLC under contract number DE-AC52-06NA25396. The work also benefited from the use of CP-SANS at Oak Ridge National Laboratory, Managed by UT-Battelle LLC for the USDOE.

REFERENCES

[1] Sasa, L.A., et al., Shear-Induced Metastable States of End-Grafted Polystyrene. *Physical Review E: Soft Matter Physics*, 2011. 84(2): p. 021803.
 [2] Hjelm, R.P., et al., Interrelation of molecule scale polymer melt response to shear and rheology in the non-linear rheological domain, in 13th Fall Rubber Colloquium: November 6-8, 2018, Hannover, Germany. 2018, Deutsches Institut für Kautschuktechnologie e.V., 2018: Hannover, Germany.
 [3] McLeish, T.C.B., Tube theory of entangle polymers. *Advances in Physics*, 2002. 51(6): p. 1379-1527.
 [4] McLeish, T.C.B. and S.T. Milner, Engtangled dynamics of Melt Flow of Branched polymers. *Advances in Polymer Science*, 1999. 143(6): p. 197-256.
 [5] Chhabra, R.P. and J.F. Richardson, *Non-Newtonian Flow and Applied Rheology*. 2008, Boca Raton, FL: Butterworth-Heinemann.
 [6] Larsen, R.G., *The Structure and Rheology of*

Complex Fluids 1999, New York, NY: Oxford Univ. Press.

[7] Ramaswamy, H.S. and M. Marcotte, *Food Processing: Principles and Applications* 2006, Burlington, MA: CRC Press.
 [8] Tadmor, Z. and C.G. Gogos, *Principles of Polymer Processing*. 2006, Hoboken, NJ: Wiley-Interscience.
 [9] Treolar, L.R.G., *Physics of Rubber Elasticity* 1953: New York, NY, 1999); L. R. G. Treolar, *Physics of Rubber Elasticity* (Oxford.
 [10] Graham, R.S., et al., The long-chain dynamics in a model homopolymer blend under strong flow: small-angle neutron scattering and theory. *Soft Matter*, 2009. 5: p. 2383-2389.
 [11] Graham, R.S. and T.C.B. McLeish, Emerging applications for models of molecular rheology. *J. Non-Newtonian Fluid Mechanics*, 2008. 150(1): p. 11-18.
 [12] Bent, J., et al., Neutron-Mapping Polymer Flow: Scattering, Flow Visualization, and Molecular Theory. *Science*, 2003. 301: p. 1691-1695.
 [13] Dealy, J.M. and R.G. Larson, *Structure and Rheology of Molten Polymers*. 2006, Cincinnati: Hanser Gardner.
 [14] De Gennes, P.G., Reptation of a Polymer Chain in the Presnce of Fixed Obstacles. *The Journal of Chemical Physics*, 1971. 35(2): p. 572-579.
 [15] Doi, M. and S.F. Edwards, Dynamics of Concentrated Polymer Systems Part 1-Brownian Motion in the Equilibrium State. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 1978. 74: p. 1789-1801.
 [16] Doi, M. and S.F. Edwards, Dynamics of Concentrated Polymer Systems Part 2.-Molecular Motion under Flow. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 1978. 74: p. 1802-1817.
 [17] Doi, M. and S.F. Edwards, Dynamics of Concentrated Polymer Systems Part 3.-The Constitutive Equation. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 1978. 74: p. 1818-1832.
 [18] Doi, M. and S.F. Edwards, Dynamics of Concentrated Polymer Systems Part 4.-Rheological Properties. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 1979. 75: p. 38.
 [19] Doi, M. and S.F. Edwards, *The Theory of Polymer Dynamics*. 1986, New York: Oxford University Press.
 [20] Edwards, S.F., The statistical mechanics of polymerized material. *Proceedings of the Physical Society*, 1967. 92: p. 9-16.
 [21] Rubinstein, M. and R.H. Colby, *Polymer Physics*. 2003, Oxford, UK: Oxford University Press.

- [22] Likhtman, A.E., S.T. Milner, and T.C.B. McLeish, Microscopic theory for the fast flow of polymer melts. *Physical Review Letters*, 2000. 83(21): p. 4550-4553.
- [23] Marrucci, G., Dynamics of entanglements: A non-linear model consistent with the Cox-Merz rule. *Journal of Non-Newtonian Fluid Mechanics*, 1996. 62: p. 279-289.
- [24] Mead, D.W., R.C. Larson, and M. Doi, a molecular theory for fast flows of entangled polymers. *Macromolecules*, 1998. 31: p. 7895-7914.
- [25] Graham, R.S., et al., Microscopic Theory of Linear, entangle polymer chains under rapid deformation including chain stretch and convective constraint release. *Journal of Rheology*, 2003. 47: p. 1171-1200.
- [26] Cates, M.E., T.C.B. McLeish, and G. Marrucci, The Rheology of Entangled Polymers at Very High Shear Rates. *Europhysics Letters*, 1993. 21(4): p. 451-456.
- [27] Likhtman, A.E. and T.C.B. McLeish, Quantitative Theory for Linear Dynamics of Linear Entangled Polymers. *Macromolecules*, 2002. 35(16): p. 6332-6343.
- [28] Collis, M.W., et al., Constriction flows of monodisperse linear entangled polymers: Multiscale modeling and flow visualization. *Journal of Rheology*, 2005. 49(3): p. 501-522.
- [29] Kirkwood, K.M., et al., Stress Relaxation of Comb Polymers with Short Branches. *Macromolecules*, 2009. 42: p. 9592-9608.
- [30] Oberhauser, J.P., K. Pham, and L.G. Leal, Rheo-optical studies of the response of entangled polymer solutions to step changes in shear rate. *Journal of Rheology*, 2004. 48(6): p. 1229-1249.
- [31] Tezel, A.K., L.G. Leal, and T.C.B. McLeish, Rheo-Optical Evidence of CCR in an Entangled Four-Arm Star. *Macromolecules*, 2005. 48(4): p. 1451-1455.
- [32] Wischniewski, A., et al., Molecular Observation of Contour-Length Fluctuations Limiting Topological Confinement in Polymer Melts. *Physical Review Letters*, 2002. 88(5): p. 058301.
- [33] Glomann, T., et al., Unified Description of the Viscoelastic and Dielectric Global Chain Motion in Terms of the Tube Theory. *Macromolecules*, 2011. 44: p. 7430-7437.
- [34] Bent, J., R.W. Richards, and T.D. Gough, Recirculation cell for the small-angle neutron scattering investigation of polymer melts in flow. *Review of Scientific Instruments*, 2003. 74(9): p. 4052-4057.
- [35] Boué, F., et al., Polymer coil relaxation in uniaxially strained polystyrene observed by small angle neutron scattering. *Journal de Physique*, 1982. 43(1): p. 137-148.
- [36] Boué, F., M. Nierlich, and K. Osaki, Dynamics of Molten Polymers on the Molecular Scale. *Faraday symposia of the Chemical Society*, 1983. 18: p. 83-102.
- [37] Muller, R., J.J. Pesce, and C. Picot, Chain conformation in sheared polymer melts as revealed by SANS. *Macromolecules*, 1993. 26: p. 4356-4362.
- [38] Blanchard, A., et al., Small Angle Neutron Scattering Observation of Chain Retraction after a Large Step Deformation. *Physical Review Letters*, 2005. 95(16): p. 166001.
- [39] Graham, R.S., et al., Measuring and Predicting the Dynamics of Linear Monodisperse Entangled Polymers in Rapid Flow through an Abrupt Contraction. A Small Angle Neutron Scattering Study. *Macromolecules*, 2006. 39(7): p. 2700-2709.
- [40] Hassager, O., et al., Stress and neutron scattering measurements on linear polymer melts undergoing steady elongational flow. *Rheologica Acta*, 2012. 51: p. 385-394.
- [41] Ruocco, N., et al., Microscopic relaxation processes in branched-linear polymer blends by Rheo-SANS. *Macromolecules*, 2013. 46: p. 9122-9133.
- [42] Desai, P.S., et al., Challenging tube and slip-link models: Predicting the linear rheology of blends of well-characterized star and linear 1,4-polybutadienes. *Macromolecules*, 2016. 49(13): p. 4964-4977.
- [43] Milner, S.T., *Polymer Brushes*. Science, 1991. 251(4996): p. 905-914.
- [44] Zhao, B. and W.J. Brittain, Polymer brushes: surface-immobilized macromolecules. *Progress in Polymer Science*, 2000. 25(5): p. 677-710.
- [45] De Gennes, P.G., Conformations of polymers attached to an interface *Macromolecules*, 1980. 13: p. 1069-1075.
- [46] Migler, K.B., H. Hervet, and L. Leger, Slip-transition of polymer melt under shear stress. *Physical Review Letters*, 1991. 70(3): p. 287-290.
- [47] Sternstein, S.S. and A.-J. Zhu, Reinforcement mechanism of nanofilled polymer melts as elucidated by nonlinear viscoelastic behavior. *Macromolecules*, 2002. 35: p. 7262-7276.
- [48] Sasa, L.A., et al., The LANSCE Neutron Rheometer in the Cone and Plate Geometry to Examine Anchored Polymers/polymer Melt Interfaces via Neutron Reflectivity. *Review of Scientific Instruments*, 2010. 81(5): p. 055102.
- [49] Korolkovas, A., et al., Polymer Brush Collapse under Shear Flow. *Macromolecules*, 2017. 50: p. 1215-1224.
- [50] Yearley, E.J., et al., The Couette configuration of the Los Alamos Neutron Science Center neutron rheometer for the investigation of polymers in the bulk with small-angle neutron scattering. *Review of Scientific Instruments*, 2010. 81: p. 045109.
- [51] Andriano, L.T., et al., Microstructural Characterization of a Star-Linear Polymer Blend under Shear Flow by using Rheo-SANS. *Journal of Rheology*, 2020. 63(3): p. 663-672.
- [52] Hjelm, R.P., et al., Challenges and Opportunities for SANS Instruments at Brighter Pulsed Spallation Neutron Sources, in ICANS-XVI: 16th Meeting of the International Collaboration on Advanced Neutron Sources, G. Mank and H. Conrad, Editors. 2003, Forschungszentrum Jülich GmbH, Jülich, Germany Düsseldorf-Neuss, Germany. p. 177-183.
- [53] Seeger, P.A., R.P. Hjelm, and M.J. Nutter, The Low-Q Diffractometer at the Los Alamos Neutron Scattering Center. *Molecular Crystals Liquid Crystals*, 1990. 180: p. 101-117.
- [54] Mhether, V. and L.A. Archer, Slip in entangled polymer solutions. *Macromolecules*, 1998. 31: p. 6639-6649.
- [55] Sanchez-Reyes, J. and L.A. Archer, Shear Banding in Molecular Dynamics of Polymer Melts. *Langmuir*, 2003. 19(8): p. 3304-3312.
- [56] McKinley, G.H., P. Pakdel, and A. Öztekin, Rheological and geometric scaling of purely elastic flow instabilities. *Journal of Non-Newtonian Fluid Mechanics*, 1996. 67: p. 19-47.
- [57] Muller, S.J., Elastically-influenced instabilities in Taylor-Couette and other flows with curved streamlines: a review. *Korea-Australia Rheological Journal*, 2008. 20(3): p. 117-125.
- [58] Pakdel, P. and G.H. McKinley, Elastic instability in curved streamlines. *Physical Review Letters*, 1996. 77(12): p. 2459-2462.
- [59] Hjelm, R.P., The Resolution of TOF Low-Q Diffractometers: Instrumental, Data Acquisition and Reduction Factors. *Journal of Applied Crystallography*, 1988. 21: p. 618-628.
- [60] Seeger, P.A. and R.P. Hjelm, Small-Angle-Neutron Scattering at Pulsed Spallation Sources. *Journal of Applied Crystallography*, 1991. 24: p. 467-478.
- [61] Hsieh, H. and R.P. Quirk, *Anionic Polymerization: Principles and Practical Applications* 1996, New York: Dekker.
- [62] de Gennes, P.-G., *Scaling Concepts in Polymer Physics* 1979, Ithica, New York: Cornell University Press.
- [63] Ianniruberto, G. and G. Marrucci, On compatibility of the Cox-Merz rule with the model of Doi and Edwards. *Journal of Non-Newtonian Fluid Mechanics*, 1996. 65: p. 241-246.
- [64] Milner, S.T. and T.C.B. McLeish, Repetition and Contour-Length Fluctuations in Melts of Linear Polymers. *Physical Review Letters*, 1998. 81(3): p. 725-728.
- [65] Rubinstein, M. and R.H. Colby, Self-consistent theory of polydisperse entangled polymers: Linear viscoelasticity of binary blends. *Journal of Chemical Physics*, 1988. 89(8): p. 5291-5307.