Multiple Dynamic Processes Contribute to the Complex Steady Shear Behavior of Cross-Linked Supramolecular Networks of Semidilute Entangled Polymer Solutions

Donghua Xu and **Stephen L. Craig**[*]
Department of Chemistry and Center for Biologically Inspired Materials and Material Systems, Duke University, Durham, North Carolina 27708-0346, USA

Abstract

Molecular theories of shear thickening and shear thinning in associative polymer networks are typically united in that they involve a single kinetic parameter that describes the network — a relaxation time that is related to the lifetime of the associative bonds. Here we report the steady-shear behavior of two structurally identical metallo-supramolecular polymer networks, for which single-relaxation parameter models break down in dramatic fashion. The networks are formed by the addition of reversible cross-linkers to semidilute entangled solutions of PVP in DMSO, and they differ only in the lifetime of the reversible cross-links. Shear thickening is observed for cross-linkers that have a slower dissociation rate (17 s^{-1}), while shear thinning is observed for samples that have a faster dissociation rate (ca. 1400 s^{-1}). The difference in the steady shear behavior of the unentangled vs. entangled regime reveals an unexpected, additional competing relaxation, ascribed to topological disentanglement in the semidilute entangled regime that contributes to the rheological properties.

Keywords

networks; rheology; supramolecular structures

Associative polymers are used as rheology modifiers in a wide range of applications, including paints and coatings, cosmetics, pharmaceuticals, and oil drilling.[1,2] Underlying the utility of associative polymers is their rich rheological behavior, in particular non-Newtonian properties such as shear thickening or shear thinning. Extensive experimental and theoretical research has therefore been devoted to the molecular origin of shear thickening and shear thinning behavior,[3–8] which likely vary from one system to another. While a comprehensive molecular picture remains elusive, however, the theories associated with shear thickening and shear thinning are typically united in that they involve a single kinetic parameter that describes the network — a relaxation time that is related to the lifetime of the associative bonds.[5–8] Here we present an associative polymer network for which all single-relaxation parameter models break down in dramatic fashion, providing direct evidence for a competition between relaxation modes in semidilute entangled associative polymer solutions that unites shear thickening and shear thinning behavior on a continuum of network responses to steady shear.

[*]To whom correspondence should be addressed. stephen.craig@duke.edu.

At the core of this investigation is a conceptually simple, but practically useful, method for probing the contributions of molecular reversibility to the rheological properties of polymers and polymer networks. [9,10] Associative polymer networks are formed by mixing bisfunctional N,C,N-pincer Pd(II) complexes **1a–c** (Figure 1) and poly(4-vinylpyridine) (PVP) in dimethylsulfoxide (DMSO). Each of the two Pd atoms in **1** reversibly coordinates to the PVP pyridine groups, providing an associative cross-linker. For a given concentration of PVP and **1**, the extent of cross-linking is determined by the association constant K_{eq} of the Pd-pyridine coordination bond.[8] For **1a–c**, K_{eq} is effectively constant at ~ 30 M^{-1}, and so, too, is the number of cross-links formed, as evidenced by the constant high-frequency elastic modulus measured by low-strain oscillatory rheology.[8] The dissociation rate constant k_d for the **1**•pyridine bonds (and, therefore, the **1**•PVP cross-links), however, depends on the sterics associated with the alkyl substituents on the nitrogen atoms in **1a–c**, and it can be varied independently of K_{eq} from 17 s^{-1} for **1b** to 1450 and 1355 s^{-1} (Figure S1 in supporting material) for **1a** and **1c**, respectively. [9,11]

The methodology facilitates a direct investigation of the contributions of cross-linker dissociation to the rheological behavior of the metallo-supramolecular polymer network. For example, the linear oscillatory rheology of **1**•PVP has been shown previously to scale with the values of k_d measured independently on small molecular model systems.[12] Similar scaling behavior has been observed for shear thickening under steady shear;[8] characteristic behavior from ref. [8] for the **1a**•PVP and **1b**•PVP networks in semi-dilute unentangled concentrations of PVP (0.1 g/mL) is reproduced for convenience in Figure 2. The superposition of the rheological data upon scaling by k_d is consistent with transient network models (linear oscillatory rheology) and models for shear thickening based on either network reorganization or non-Gaussian overstretching (non-Newtonian steady shear).[8]

Here we report that, in marked contrast to our previous studies[8] and conventional models, these simple scaling relationships break down in the steady shear behavior of **1**•PVP networks formed in semi-dilute entangled PVP/DMSO solutions. The breakdown requires the contributions of a mechanism that is fundamentally different from that underlying the physics in previous studies.[8] The semi-dilute entangled regime applies to concentrations of PVP greater than ~ 0.16 g/mL,[8] and simple scaling laws estimate that the average number of entanglements per polymer chain varies from 1 to $\sim$1.9 for concentrations of 0.16 g/mL to 0.26 g/mL (see Supporting Information). For 0.22 g/mL and 0.26 g/mL PVP/DMSO solutions (Figure 3), the steady shear viscosity of samples with **1b** exhibits four flow regimes as the shear rate increases. In order of increasing shear rate, these regimes are: Newtonian, local shear thinning (comprising points with a negative slope in viscosity with respect to shear rate), local shear thickening (positive slope in viscosity with respect to shear rate) and dramatic shear thinning (corresponding to network rupture and/or ejection of samples out of geometry[8]). For simplicity, the preceding terms will be used as employed above, to distinguish these flow regimes from general shear thinning (above a critical shear rate, viscosity is less than the zero shear viscosity) and shear thickening (viscosity at a critical shear rate is greater than the zero shear viscosity). In contrast, otherwise identical samples made with **1a** do not show a local shear thickening regime. At lower PVP concentrations of 0.160 – 0.191 g/mL, modest shear thickening is observed for samples with either **1a** or **1b**, whereas samples in the semidilute unentangled regime ([PVP] < 0.16 g/mL) exhibit shear thickening only, as previously reported [8] and shown again here for comparison. That the differential behavior of the **1a**• PVP solutions is due to the cross-linker dissociation kinetics is confirmed by studies on PVP networks formed with cross-linker **1c**, the k_d of which is very close to that of cross-linker **1a**. The **1c**•PVP network shows shear thinning behavior similar to that of **1a**• PVP at ~ 0.26 g/mL of PVP (Figure S2 in supporting material).

A single time scale model [5–8] clearly cannot adequately account for the opposing effects (shear thinning vs. shear thickening) in Figure 3. Some theories use multiple time scales to characterize the competition between shear thickening and shear thinning under steady shear. Vaccaro et al., for example, have shown that stress-induced detachment of cross-linkers under non-Gaussian stretching of active polymer chain segments can lead to divergent outcomes.[4] But we have previously reported that shear thickening in these networks is dominated not by non-Gaussian over-stretching, but by the shear-induced conversion of intramolecular cross-linkers to intermolecular cross-linkers.[8] In addition, single-molecule force spectroscopy studies suggest that the effect of force-induced dissociation should also scale with k_d.[13] Tripathi et al. have examined a model in which the competition between shear thinning and shear thickening is explained by differences in network structure,[14] but such considerations do not apply to these networks, in which the equilibrium distribution of states for **1a** and **1b** are indistinguishable.[8]

The most likely explanation for the divergent behavior in the semidilute entangled regime is the presence of topological entanglements in addition to associative cross-linkers.[15,16] We have previously reported that shearing the latter leads to network reorganization and shear thickening,[8] but shearing the former results in a depletion of entanglements.[17] It is reasonable, therefore, that there are two time scales at play: one due to dissociation of cross-linkers, and a second due to disentanglement of polymer chains. While the reptation time of entangled associative polymer chains in the linear rheological regime is proportional to k_d of cross-linkers,[18,19] our results suggest that the disentanglement rate of polymer chains under nonlinear steady shear is not. The shear rate-dependent contributions of these two opposing factors would account for the breakdown of simple scaling laws observed here. This competition between two time scales has been speculated before, but interpretation of the data is somewhat complicated by the changes in structure that accompany changes in concentration of associative polymer solutions.[15] Here, the competition between multiple time scales is established by keeping the structure of the network constant; only k_d of cross-linkers changes. The competitive interplay of cross-linker kinetics and polymer dynamics has been examined previously in contexts other than shear thinning and shear thickening, [18,19] and, with the recent advances in supramolecular polymers, it is drawing increasing interest.[20] The networks described here are well suited for further, ongoing investigations into the underlying physics.

Experimental section

Dimethyl sulfoxide (DMSO) and poly(4-vinylpyridine) (PVP), $M_w = 60,000$, were used as received from Aldrich. Cross-linkers of [2,3,5,6-tetrakis{(dimethylamino)methy}phenylene-1,4-bis(palladiumtrifluoromethanesulfonate)] (**1a**), [2,3,5,6-tetrakis{(diethylamino)methyl}phenylene-1,4-bis(palladiumtrifluoromethanesulfonate)] (**1b**) and [2,3,5,6-Tetrakis(methylpiperidyl)phenylene-1,4-bis(palladiumtrifluoromethanesulfonate)] (**1c**) were synthesized as reported elsewhere.[11] Samples are prepared by mixing solutions of PVP and cross-linkers. Details can be found in a previous paper.[8] Samples with 2% molar ratios of palladium atoms (two per cross-linker) to pyridine nitrogens in PVP were used – above the critical concentration for forming a network (gel point).[8] All rheological data were obtained on an AR G2 rheometer (TA Instruments, USA) with cone-plate geometry (diameter of 20 mm, cone angle of 2°, truncation height of 49 μm.). Oscillatory frequency sweeps were carried out within the linear region.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

References

1. Berret JF, Calvet D, Collet A, Viguier M. Fluorocarbon Associative Polymers. Curr Opin Colloid Interface Sci. 2003; 8:296–306.

2. Pellens L, Corrales RG, Mewis J. General Nonlinear Rheological Behavior of Associative Polymers. J Rheol. 2004; 48:379–393.

3. Klucker R, Candau F, Schosseler F. Transient Behavior of Associating Copolymers in a Shear Flow. Macromolecules. 1995; 28:6416–6422.

4. Vaccaro A, Marrucci G. A Model for the Nonlinear Rheology of Associating Polymers. J Non-Newtonian Fluid Mech. 2000; 92:261–273.

5. Marrucci G, Bhargava S, Cooper SL. Models of Shear-Thickening Behavior in Physically Cross-Linked Networks. Macromolecules. 1993; 26:6483–6488.

6. Ma SX, Cooper SL. Shear Thickening in Aqueous Solutions of Hydrocarbon End-Capped Poly(ethylene oxide). Macromolecules. 2001; 34:3294–3301.

7. Indei T, Koga T, Tanaka F. Theory of Shear-Thickening in Transient Networks of Associating Polymers. Macromol Rapid Commun. 2005; 26:701–706.

8. Xu D, Hawk J, Loveless DM, Jeon SL, Craig SL. Mechanism of Shear Thickening in Reversibly Cross-Linked Supramolecular Polymer Networks. Macromolecules. 2010; 43:3556–3565. [PubMed: 20479956]

9. Yount WC, Juwarker H, Craig SL. Orthogonal Control of Dissociation Dynamics Relative to Thermodynamics in a Main-Chain Reversible Polymer. J Am Chem Soc. 2003; 125:15302–15303. [PubMed: 14664569]

10. Yount WC, Loveless DM, Craig SL. Small-Molecule Dynamics and Mechanisms Underlying the Macroscopic Mechanical Properties of Coordinatively Cross-Linked Polymer Networks. J Am Chem Soc. 2005; 127:14488–14496. [PubMed: 16218645]

11. Jeon SL, Loveless DM, Yount WC, Craig SL. Thermodynamics of Pyridine Coordination in 1,4-Phenylene Bridged Bimetallic (Pd, Pt) Complexes Containing Two N,C,N'Motifs, 1,4-M2-[C6(CH2NR2)4-2,3,5,6]. Inorg Chem. 2006; 45:11060–11068. [PubMed: 17173466]

12. Loveless DM, Jeon SL, Craig SL. Rational Control of Viscoelastic Properties in Multicomponent Associative Polymer Networks. Macromolecules. 2005; 38:10171–10177.

13. Kersey FR, Yount WC, Craig SL. Single-Molecule Force Spectroscopy of Bimolecular Reactions: System Homology in the Mechanical Activation of Ligand Substitution Reactions. J Am Chem Soc. 2006; 128:3886–3887. [PubMed: 16551077]

14. Tripathi A, Tam KC, McKinley GH. Rheology and Dynamics of Associative Polymers in Shear and Extension: Theory and Experiments. Macromolecules. 2006; 39:1981–1999.

15. English RJ, Gulati HS, Jenkins RD, Khan SA. Solution Rheology of a Hydrophobically Modified Alkalisoluble Associative Polymer. J Rheol. 1997; 41:427–444.

16. Regalado EJ, Joseph Selb J, Candau F. Viscoelastic Behavior of Semidilute Solutions of Multisticker Polymer Chains. Macromolecules. 1999; 32:8580–8588.

17. Milner ST, McLeish TCB. Reptation and Contour-Length Fluctuations in Melts of Linear Polymers. Phys Rev Lett. 1998; 81:725–728.

18. Leibler L, Rubinstein M, Colby RH. Dynamics of Reversible Networks. Macromolecules. 1991; 24:4701–4707.

19. Rubinstein M, Semenov AN. Dynamics of Entangled Solution of Associating Polymers. Macromolecules. 2001; 34:1058–1068.

20. Hoy RS, Fredrickson GH. Thermoreversible Associating Polymer Networks. I. Interplay of Thermodynamics, Chemical Kinetics, and Polymer Physics. J Chem Phys. 2009; 131:224902. [PubMed: 20001079]

1a R= Me

1b R= Et

1c $R_2 = -(CH_2)_5-$

Figure 1.
Schematic picture of networks formed from PVP chains and cross-linking bimetallic compounds (**1a–c**). Two triflate counterions, $CF_3SO_3^-$, are not shown.
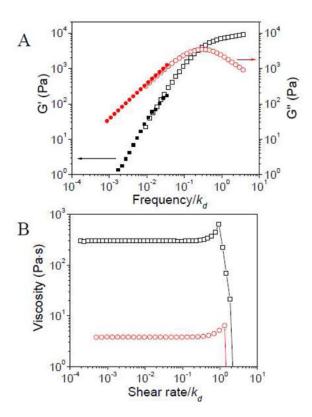
Figure 2.
Scaling of linear (A) and non-linear (B) rheology in the semi-dilute unentangled regime. (A) Storage (G') and loss (G'') moduli versus scaled frequency for ~0.1 g/mL PVP/DMSO solution with 2% of **1a** or **1b**. Filled and unfilled symbols represent networks formed from cross-linker **1a** and **1b**, respectively. (B) Steady shear viscosity versus scaled shear rate for ~0.1 g/mL PVP/DMSO solution with 2% of **1a** or **1b**. Circles and squares represent networks formed from cross-linker **1a** and **1b**, respectively. T = 25 °C. Data taken from ref. [8].
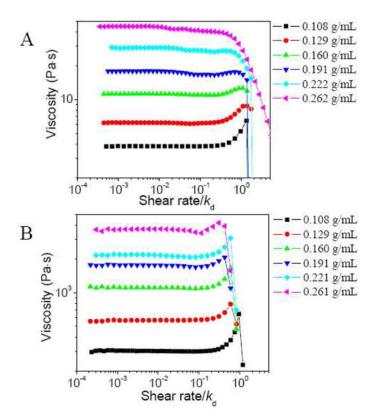
Figure 3.
Steady shear viscosity versus scaled shear rate for different concentration of PVP/DMSO solution with 2% of **1a** (A) or **1b** (B) at 25 °C.