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Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interactions

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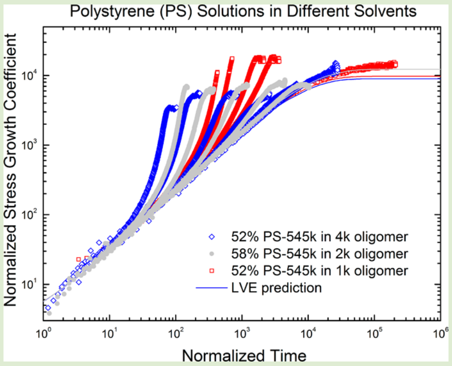
ABSTRACT: We compare the linear and nonlinear rheological response of three entangled polystyrene solutions with the same concentration of polymer, but diluted using different solvents. The three solutions have exactly the same physical tube model parameters when normalized to the same time scale. Although the three solutions behave identically in small amplitude oscillatory shear flow, they behave markedly different in large strain extensional flow. The experimental observations presented here directly demonstrate that the tube model and its governing parameters are insufficient to describe the nonlinear rheological behavior of entangled polymer solutions. We introduce a new hypothesis that relates the observed nonlinear behavior of three different polymer solutions to the existence of nematic interactions between polymer−solvent and polymer−polymer molecules.



Over the past two decades, there has been an unremitting effort on modifying the tube model and reptation theory[1] to describe the viscoelastic behavior of entangled polymer chains. The important molecular mechanisms added to the original tube model include contour length fluctuations[2]/constraint release[3] to describe linear viscoelasticity and chain stretch[4] /convective constraint release[5]/finite extensibility[6] to describe nonlinear viscoelasticity.

Although the modified tube model quantitatively explains different aspects of the linear viscoelastic response of entangled polymer chains, experiments indicate that the modified tube model does not describe well the nonlinear viscoelastic response in extensional flow even for the simplest case of monodisperse linear polymer melts.[7] For example, an additional parameter λ_{max}, the maximum stretch ratio of the entanglement segment, is insufficient to capture observed differences between concentrated polymer solutions and melts.[8] It is evident that the current tube model is missing key physics to describe the rheological behavior of both concentrated polymer solutions and melts. One key component that may be missing is the effect of nematic interactions between polymer−solvent and polymer−polymer molecules.

Local correlations in the orientation of neighboring molecules have been shown to exist both experimentally and theoretically for stretched polymer networks[9] and polymer melts and blends via such methods as double-quantum NMR,[10a] infrared and ultraviolet dichroism,[10b,c] statistical mechanics,[10d,e] and molecular dynamics.[10f] It is clear from this body of work that the alignment of polymer molecules induces neighboring molecules, solvent and/or polymer, to be aligned by nematic interactions.

Theoretically, the tube model predicts that such nematic interactions alter the stress-optic coefficient but predicts no change in the overall measured stress.[10d,e] Nematic interaction potentials have been included in Rouse dynamics, but while the effect on polymer chain orientation is predicted to be large, the effect on linear viscoelastic properties is predicted to be small.[10g] Recent simulation results[11] suggest that an important physical parameter is the monomeric friction between a polymer chain and the surrounding molecules, which depends on stretching and orientation of chain segments. Indeed, local friction is expected to be influenced by orientation of the molecules involved.

In this letter, we consider the influence of several solvents on the linear and nonlinear rheological response of concentrated polymer solutions in extensional flow. We prepared three polymer solutions with equal concentration of the same polymer but diluted with three different solvents. The three solutions have the same tube model parameters, as discussed later. We compare them under the same time scale and show that they behave identically in linear rheology but remarkably different in nonlinear extensional rheology, demonstrating the influence of solvent−polymer interactions not accounted for in the current tube theory.

Three polymer solutions were made from a polystyrene diluted in three different styrene oligomers. The polystyrene PS-545k was synthesized by living anionic polymerization.[8] It

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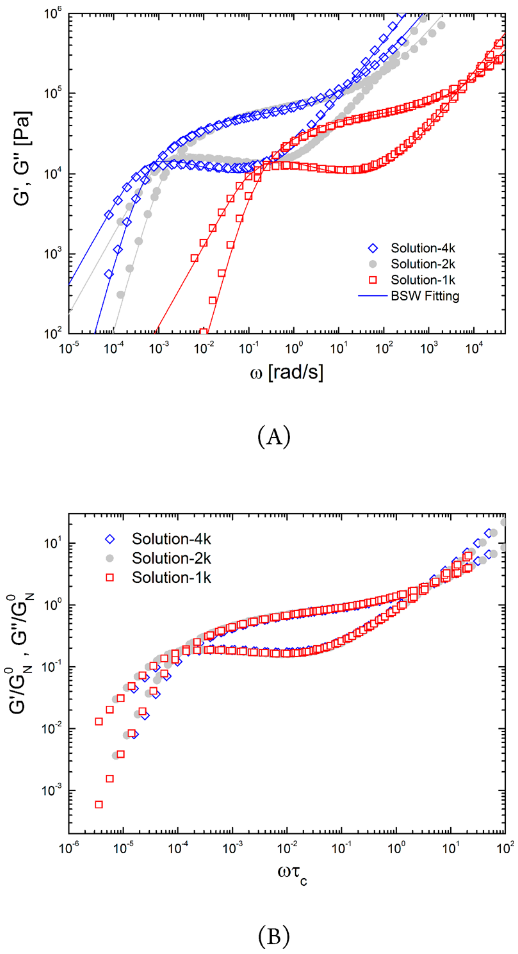
has a weight average molecular weight M_w = 545 000 g mol^{-1} and a polydispersity index PDI = 1.12. The three styrene oligomers OS-4k, OS-2k, and OS-1k were purchased from Sigma–Aldrich. OS-4k has M_w = 4290 g mol^{-1} and PDI = 1.04; OS-2k has M_w = 1920 g mol^{-1} and PDI = 1.08; and OS-1k has M_w = 972 g mol^{-1} and PDI = 1.12. Solution-4k contains PS-545k diluted in OS-4k and was prepared by dissolving both components in tetrahydrofuran. The solution was recovered by precipitation in methanol. Solution-2k is the same solution of PS-545k/2k-58 in Huang et al.[8] Solution-1k which contains PS-545k diluted in OS-1k was prepared by dissolving both components in benzene, and the solution was recovered by freeze-drying. The volume fractions of PS-545k in Solution-4k and Solution-1k are both φ = 0.52. Solution-2k has a slightly higher fraction with φ = 0.58. The values of φ were confirmed using size exclusion chromatography.

The linear viscoelastic (LVE) properties of the polystyrene solutions were obtained from small amplitude oscillatory shear flow measurements using an 8 mm plate–plate geometry on an ARES-G2 rheometer from TA Instruments. The LVE data for Solution-2k are taken from Huang et al.[8] The measurements for Solution-4k were performed at 130, 150, and 170 °C, while the measurements for Solution-1k were performed at 90, 110, and 130 °C. All experiments were carried out under a nitrogen atmosphere. All data are plotted at 130 °C using the time–temperature superposition procedure. Figure 1A shows the measured LVE data fitted with the continuous Baumgaertel–Schausberger–Winter (BSW) relaxation spectrum[12] for the three solutions at 130 °C. The values of n_e (predicted to be 1/4 in the tube theory[13]) and n_g are fixed to 0.23 and 0.70, respectively.[14] The plateau modulus G_N^0, the crossover relaxation time τ_c, and the maximum relaxation time τ_{max} are found by the least-squares fitting to the LVE data. The BSW parameters are listed in Table 1. Note that the physical meaning of the individual BSW parameters is described in Huang et al.[8] The longest relaxation time of the pure oligomer OS-4k at 130 °C is in the order of 10^{-5} s, which is negligible compared with the maximum relaxation time τ_{max} for the solution in Table 1. OS-2k and OS-1k have even faster relaxation times at 130 °C.

The nonlinear viscoelastic properties of polystyrene solutions were obtained from stress–strain measurements under uniaxial extensional flow. The measurements were performed using a filament stretching rheometer (FSR).[15] The FSR is operated in controlled strain rate mode.[16] Before the elongational measurements, all the polystyrene samples were molded into cylindrical test specimens under vacuum with a fixed radius R_0 = 2.7 mm. The samples were pressed and annealed for 15 min at 150 °C (Solution-4k) and 110 °C (Solution-1k) under vacuum to ensure that the polymer chains were completely relaxed. The initial length L_0 of the cylindrical test specimens varied between 1.3 and 1.6 mm, giving an aspect ratio $\Lambda_0 = L_0/R_0$ between 0.48 and 0.59. All the samples were prestretched to a radius R_p ranging from 1.5 to 2.5 mm at either 160 °C (Solution-4k) or 120 °C (Solution-1k) prior to the elongational experiments.[8] After prestretching, the temperature was decreased to either 130 °C (Solution-4k) or 90 °C (Solution-1k) for the extensional stress measurements. In the evaluation of the startup of extensional stress growth coefficient, $\bar{\eta}^+$, the method from Rasmussen et al.[17] was applied. At elevated temperatures the samples were kept under a nitrogen environment. The experimental data for Solution-2k are again taken from Huang et al.[8]



(A)

(B)

Figure 1. (A) LVE data fitted with the BSW spectrum (solid lines) for Solution-4k, Solution-2k, and Solution-1k at 130 °C. (B) Comparison of the LVE data under dimensionless parameters for Solution-4k, Solution-2k, and Solution-1k. The data of Solution-2k are taken from ref 8.

According to the unmodified tube model, an entangled polymer melt or solution is characterized by three independent parameters: a tube diameter (a), the number of entanglements per chain (Z), and the equilibration time of one entanglement (τ_c). The remaining tube model parameters, such as the entanglement molecular weight (M_e), the plateau modulus (G_N^0), the reptation time (τ_d), and the Rouse time (τ_R) can all be determined from the three independent parameters. For the case of an entangled polymer solution, the solvent is treated as a Newtonian medium and assumed to relax sufficiently fast that it can be treated as a material without structure. The addition of solvent increases the tube diameter and changes the entanglement equilibration time. Therefore, the tube model predicts that concentrated polymer solutions and polymer melts with the same value of Z have identical linear viscoelastic responses, when the modulus is scaled by G_N^0 and the frequency scaled by τ_c, as previously observed by Huang et al.[8]

Experiments[8] indicated that the entanglement molecular weight M_e of concentrated polystyrene solutions is given by $M_e = M_e(1)\varphi^{-1}$,[8] where $M_e(1)$ is the entanglement molecular weight of the polymer melt and φ is the volume fraction of the polymer in the solution. We take $M_e(1)$ = 13 300 g mol^{-1} for polystyrene melts.[7b] The number of entanglements per chain is calculated as $Z = MM_e^{-1}$, where M is the molecular weight of

Table 1. Material Properties Obtained from the BSW Spectrum at 130 °C

solutions	T_g [°C]	Z	M_e [g mol^{-1}]	n_e	n_g	$G_N{}^0$ [Pa]	τ_c [s]	τ_{max} [s]	τ_R [s]
Solution-4k	98.6	21.3	25600	0.23	0.70	68900	0.20	3180	92.5
Solution-2k	91.0	23.8	22900	0.23	0.70	84100	0.051	1110	29.1
Solution-1k	54.0	21.3	25600	0.23	0.70	67600	0.00057	9.85	0.26

the polymer. The Rouse time is defined as $\tau_R = Z^2\tau_c$.[8] Since Solution-4k, Solution-2k, and Solution-1k are diluted from the same polymer to the same volume fraction, they have the same values of M_e and Z, which are listed in Table 1. Note that the fitted plateau moduli from the LVE data for the three solutions are approximately equal, confirming that all the solutions have the same M_e.[8]

Due to the difference in solvent, the solutions do not have the same glass transition temperature (T_g), and therefore when compared at the same temperature they have different time scales. To account for this difference in time scales, the LVE data in Figure 1A for Solution-1k, Solution-2k, and Solution-4k are normalized vertically and horizontally by $G_N{}^0$ and τ_c, respectively. Figure 1B shows the normalized LVE data for the three polymer solutions.[8] It is evident from Figure 1B that as predicted by the tube model the three solutions have identical LVE responses. This signifies that there exists a master LVE curve for each value of Z independent of the solvent molecular structure. Furthermore, it would appear that the tube model is sufficient to describe polymer melts and solutions near equilibrium.

We now investigate if the success of the tube model in the linear regime can be extended into the nonlinear regime where the polymer chains are highly oriented and stretched. Figure 2 compares the normalized nonlinear rheological behavior of the three polystyrene solutions in extensional flow, normalized in the same way as shown in Figure 1B. The solid lines in Figure 2 are the LVE predictions. Departure from the LVE signifies nonlinear strain hardening. The normalized stretch rate, also known as the Weissenberg number, is defined as $Wi_R = \dot{\epsilon}\tau_R$, where $\dot{\epsilon}$ is the strain rate. It is clear from Figure 2 that the three solutions show identical linear behavior in extension but remarkably different nonlinear behavior. For example, Solution-1k is significantly more strain hardening than Solution-4k, even though they have the same parameters in classical tube model including the nonlinear parameter λ_{max}.

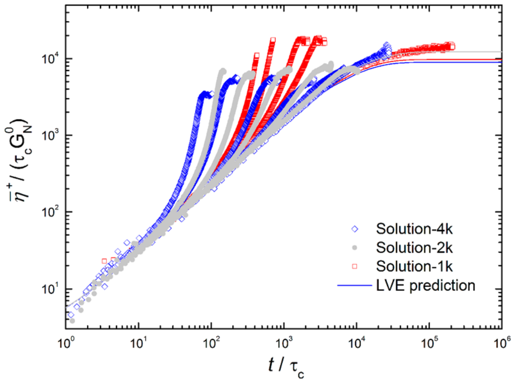


Figure 2. Comparison of the normalized extensional stress growth coefficient as a function of the normalized time for Solution-4k, Solution-2k, and Solution-1k in the startup of extensional flow for two concentrated polymer solutions. Weissenberg number ($Wi_R = \dot{\epsilon}\,\tau_R$) for Solution-4k (from left to right): 18.5, 9.25, 2.77, 0.925, 0.277, 0.0925; Wi_R for Solution-2k (from left to right): 13.10, 6.69, 2.21, 0.67, 0.22; Wi_R for Solution-1k (from left to right): 3.00, 1.93, 0.965, 0.579, 0.00290. The data for Wi_R = 3.00 and 1.93 were terminated before steady state because of filament rupture. Experiments in the interval 0.579−0.00290 are not shown since the filaments lost symmetry. The data of Solution-2k are taken from ref 8.

The effect is more clearly seen in Figure 3 which compares the normalized steady-state extensional viscosity of the three solutions. A polystyrene melt (PS-285k) with the same number of entanglements per chain (Z) as the three solutions is also compared in Figure 3. The data of PS-285k are taken from Huang et al.[8] In Figure 3, all systems behave differently. For example, when $Wi_R > 1$, the steady-state viscosities of the three polymer solutions reach two distinct plateau regions, and the viscosity of the polymer melt monotonically decreases.

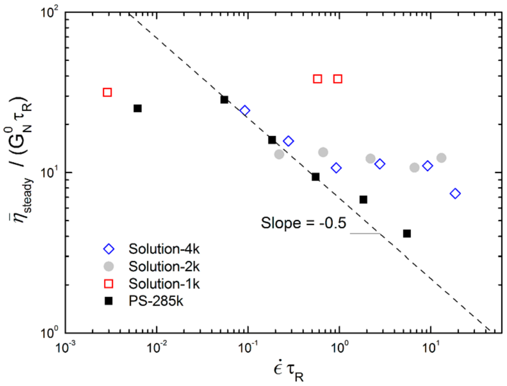


Figure 3. Comparison of the normalized steady-state extensional viscosity as a function of the Weissenberg number for the polystyrene solutions. The data of PS-285k and Solution-2k are taken from ref 8. All the samples have within 12% the same number of entanglements per chain.

One might suggest that the difference in the measured nonlinear response between the three solutions can be explained by the orientation-induced reduction of monomeric friction suggested by Yaoita et al. and Ianniruberto et al.[11] However, the Yaoita model assumes that the solvent stays isotropic under all conditions of interest, and the friction reduction is only related to the anisotropy of the polymer molecules. This implies that the model predicts all three solutions to have the same friction coefficient and thus nonlinear rheological response. Consequently, the observed difference of the three solutions suggests that the solvent molecules are not isotropic but contribute in various degrees to the anisotropy via alignment. Since the three solvent molecules have relaxation times much smaller than time scales of the flow, the alignment is assumed to occur via nematic interactions.[10] The size of the Kuhn segment for the polystyrene melt is about 610 g mol^{-1}.[8] Thus, the solvents in the three solutions, OS-4k, OS-2k, and OS-1k, contain about 7.0, 3.1, and 1.6 Kuhn segments, respectively. The nematic interactions are expected to be weak when the length of the solvent molecules is close to the size of the Kuhn segment. This would explain the observation that Solution-1k is more strain hardening than Solution-4k.

In conclusion, we propose the hypothesis that nematic interactions, both polymer−solvent and polymer−polymer, are in part responsible for the nonlinear rheological response of concentrated polymer solutions and melts in strong extensional flow. This hypothesis is supported by the results presented above, whereby in the linear regime no nematic effects on the viscoelastic properties are present so that all three solutions behave identically to a polymer melt with the same number of entanglements; however, in the nonlinear regime, nematic effects are present, and the rheological behavior of polystyrene solutions depends on the chemical structure and size of the solvent molecules. These results and hypothesis are in contrast to all current tube-based models and could explain why semidilute polymer solutions (little or no nematic interactions) can be so well described by the present tube model.

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Notes

The authors declare no competing financial interest.

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