Viscometric Properties of Dilute Polystyrene/Dioctyl Phthalate Solutions

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ABSTRACT: We report viscometric data collected in a Couette rheometry on dilute, single-solvent polystyrene (PS)/dioctyl phthalate (DOP) solutions over a variety of polymer molecular weights \(5.5 \times 10^5 \leq M_w \leq 3.0 \times 10^6\) Da and system temperatures \(288 K \leq T \leq 318 K\). In view of the essential viscometric features, the current data may be classified into three categories: The first concerns all the investigated solutions at low shear rates, where the solution properties are found to agree excellently with the Zimm model predictions. The second includes all sample solutions, except for high-molecular-weight PS samples \(M_w \geq 2.0 \times 10^6\) Da, where excellent time–temperature superposition is observed for the steady-state polymer viscosity at constant polymer molecular weights. No similar superposition applies at a constant temperature but varied polymer molecular weights, however. The third appears to be characteristic of dilute high-molecular-weight polymer solutions, for which the effects of temperature on the viscosity curve are further complicated at high shear rates. The implications concerning the relative importance of hydrodynamic interactions, segmental interactions, and chain extensibility with increasing polymer molecular weight, system temperature, and shear rate are discussed. ©2006 Wiley Periodicals, Inc.

Keywords: bead-spring model; dilute polymer solution; viscometric property

INTRODUCTION

Understanding the viscometric properties of dilute polymer solutions has been pursued for more than a half century. Recent interest in such polymer systems arises from practical applications, such as ink-jet printing and spin casting, as well as for testing Brownian dynamics simulations of bead-spring or bead-rod models. Unlike their concentrated counterparts for which the effects of polymer entanglement generally predominate, the viscometric properties of dilute polymer solutions have been known to be susceptible to the effects of hydrodynamic interactions (HI), excluded volume (EV), and finite chain extensibility. To what extent the aforementioned molecular mechanisms might practically affect the rheology of dilute polymer solutions has thus become an imperative issue in experimental investigations.

As the rheology of dilute polymer solutions is concerned, the vast majority of experimental data have been reported for the so-called Boger fluid systems. Using short-chain polymer additives to promote the overall fluid elasticity, Boger fluids have been ideal sample solutions for widespread rheological applications, in addition to their capability serving as model Oldroyd-B fluids for testing benchmark constitutive equations in complex flows. The difficulty to differentiate the impact of polymer additives is, however, a notable drawback for relying on mixed-solvent Boger fluid systems. On the other hand, because of inertial or elastic instabilities commonly associated with the measurements in cone-
and-plate or parallel-plate geometries, high-shear viscometric measurements on dilute polymer solutions have relied mainly on capillary rheometry system.

Motivated by the aforementioned observations, we have recently performed systematical viscometric investigations on single-solvent (DOP) as well as mixed-solvent (DOP plus short-chain PS), nonoverlapping PS solutions within a Couette geometry. The utility of a high-viscosity solvent, DOP, makes it possible to investigate the full range, both Newtonian and non-Newtonian, of viscometric responses for dilute PS solutions over a variety of molecular weights and system temperatures. By doing so, the measured solution properties may, in general, be qualitatively compared with existing data based on capillary viscometers and, in particular, systematically analyzed in view of the impact of HI, EV, and chain extensibility in steady shear flows. In this respect, we note that recent Brownian dynamics simulations of bead-spring models have proven only partially successful in predicting a limited spectrum, we note that recent Brownian dynamics models, followed by a summary of the central findings and implication of this study.

This article is organized as follows: We first provide the experimental details, and then make some qualitative comparisons between experimental data and the predictions of bead-spring models, followed by a summary of the central findings and implication of this study.

### EXPERIMENTAL

Nearly monodisperse PS ($5.5 \times 10^5 \leq M_w \leq 3.0 \times 10^6$ Da; see detailed information in Table 1) were dissolved in cyclohexane (for contrasting purpose) or in DOP, the latter being a solvent for PS at $22 ^\circ C$. Good dispersion of the polymer chain in solution was achieved by mild and steady shaking at a constant temperature (30 or $60 ^\circ C$) for 2 weeks. Subsequent viscometric measurements were conducted in a Couette geometry (MCR500, Parr Physics; $14.36 \text{ mm inner radius and } 14.46 \text{ mm outer radius}$), with the maximum shear rate $\dot{\gamma} \approx 10^4 \text{ s}^{-1}$ estimated to be sufficiently apart from the predicted onset of flow instabilities due to fluid inertia or elasticity in a similar geometry. In addition, the measured solvent viscosity was noted to remain Newtonian for the whole range of shear rates investigated. The system temperature ($288 \text{ K} \leq T \leq 318 \text{ K}$) was controlled within the same rheometry system, and each measurement started about fifteen minutes after the controlled system had indicated thermal equilibrium. To avoid possible memory effect, consecutive measurements were separated by at least twenty minutes. Intrinsic viscometric properties were determined using a typical extrapolation to infinite dilute condition. Most of the data reported here were, however, reduced properties at finite polymer concentrations. Finally, it should be noted that the primary range of system temperatures investigated ($295 \text{ K} \leq T \leq 318 \text{ K}$) corresponds to a similar solvent quality evaluated on the basis of intrinsic viscosity data, and thus, some peculiar effects of system temperature noted at high polymer molecular weights and shear rates may be discriminated more easily.

### RESULTS AND DISCUSSION

For contrasting purpose, we have measured the specific polymer viscosity, $(\eta - \eta_s)/\eta_s$, divided by the polymer concentration, $c$, at various concentrations for a test PS/cyclohexane solution, where $\eta$ and $\eta_s$ denote the solution and the solvent viscosities, respectively. Extrapolation to zero concentration then yielded the so-called intrinsic viscosity, $[\eta]_0 := \lim_{c \to 0} (\eta - \eta_s)/c \eta_s$, where $\dot{\gamma}$ is the imposed shear rate. The result we obtained, $[\eta]_0 = 88 \text{ mL/g}$, is in close agreement with what reported in the literature. Note that cyclohexane is a typical low-viscosity solvent ($\eta_s \approx 1 \text{ cp at the room temperature}$) in comparison with DOP ($\eta_s \approx 53 \text{ cp at the room temperature}$).

### Table 1. Material Properties of the Samples Utilized in this Experiment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular Weight, $M_w$ (Da)</th>
<th>PDI</th>
<th>Producers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene, PS1</td>
<td>$5.5 \times 10^5$</td>
<td>1.04</td>
<td>Aldrich</td>
</tr>
<tr>
<td>PS2</td>
<td>$6.8 \times 10^5$</td>
<td>1.05</td>
<td>Fluka</td>
</tr>
<tr>
<td>PS3</td>
<td>$9.3 \times 10^5$</td>
<td>1.03</td>
<td>Aldrich</td>
</tr>
<tr>
<td>PS4</td>
<td>$2.0 \times 10^6$</td>
<td>1.09</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>84</td>
<td>–</td>
<td>Riedel</td>
</tr>
<tr>
<td>DOP</td>
<td>390</td>
<td>–</td>
<td>Fluka</td>
</tr>
</tbody>
</table>
According to the predictions of kinetic theory models, it can be shown that the previous disparity in solvent viscosity would imply that the longest PS relaxation time in DOP should be 50 times longer than in cyclohexane at a similar temperature and solvent quality. This essential property, in fact, makes the choice of DOP an advantageous one for viscometric experiments, especially when using a Couette rheometry for which steady shear flow with shear rates up to a few ten thousand is currently achievable. For instance, the maximum shear rate, $\dot{\gamma} \approx 10^4$ s$^{-1}$, currently achieved would require that the polymer relaxation time be well above about 1 ms to investigate the non-Newtonian responses of the sample solution. This requirement can indeed be fulfilled with DOP as a solvent for PS weights above about 0.1 M Da, as currently investigated. In what follows, we focus on the PS/DOP systems, with basic material properties summarized in Tables 1 and 2.

As the intrinsic viscosity is plotted against the polymer molecular weight, $M$, shown in Figure 1, one sees that it scales closely with $M^{1/2}$, except for the lowest temperature $T = 288$ K at which the solvent quality worsens substantially. These results are in close agreement with the Zimm model prediction under a $\theta$-condition, but differ distinctively from the Rouse model prediction, $[\eta]_0 \propto M$, which omits the effect of hydrodynamic interactions. To avoid additional complexity associated with a poor solvent condition, later we focus on the cases in which the system temperature is indicative of a nearly $\theta$-condition.

To properly interpret the experimental results, it is essential to verify whether the polymer concentrations all fall below the threshold of chain overlap. A loose criterion for estimating the overlap concentration has been given by $c^* \approx 1/[\eta]_0$. Along with the previously measured intrinsic viscosity, Table 2 compares the estimated overlap concentrations with the actual ones. It should be mentioned that the estimated value of $c^*$ based on the current intrinsic viscosity data is, in general, in good agreement with that based on a standard molecular calculation for the polymer coil size. Obviously, the sample solutions generally satisfy excellently dilute polymer condition for the range of temperatures investigated.

Figures 2–5 show the polymer viscosity (i.e., $\eta_p = \eta - \eta_s$) as functions of shear rate at four different polymer molecular weights and system temperatures. In general, non-Newtonian behavior is observable at accessibly high shear rates. An important common feature is that, except for the high-molecular-weight PS4 solution, the viscosity curves at the same polymer molecular weight but different temperatures generally fall on top of

![Figure 1](image1.png)

**Figure 1.** Intrinsic viscosity as functions of molecular weight at three different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

![Figure 2](image2.png)

**Figure 2.** Steady-state polymer viscosity for PS1 solution as functions of shear rate at four different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
each other in the power-law regime. For the case of PS4 solution (as well as for the two lowest temperatures for PS3 solution), however, a viscosity flattening is evident at high shear rates, and the viscosity curves fail to superpose since then. For dilute ultrahigh polymer solutions, in fact, an initial shear-thinning followed by a shear-thickening were sometimes observable.18,19 None of the current single-solvent PS systems clearly exhibit such a trend at accessible shear rates, however.

To facilitate a further scrutiny into the viscosity curves discussed earlier, we seek a representative polymer relaxation time to make the shear rate a reduced variable. According to the Zimm model, the longest polymer relaxation time may be estimated through the following relation along with the measured intrinsic viscosity under a \( \theta \)-condition\(^{12,14} \):

\[
\lambda = 0.766 \frac{[\eta]}{\eta_0^0.5} \frac{M}{RT} \tag{1}
\]

where \( R \) is the universal gas constant. Alternatively, the polymer relaxation time may also be roughly estimated by the reciprocal of the shear rate marking the onset of a viscosity thinning. Figure 6 compares the estimated polymer relaxation time at a \( \theta \)-temperature, \( T = 295 \) K. Recall that, with the previously obtained result for the intrinsic viscosity, \( [\eta]_0 \propto M^{0.52 \pm 0.02} \), eq 1 should yield \( \lambda \propto M^{1.52 \pm 0.02} \). A slightly different scaling law, \( \lambda \propto M^{1.70 \pm 0.09} \), appears to be obtained with...
the second method based on the viscosity curve, and the estimated polymer relaxation times are consistently smaller by a factor about four. For comparison, we mention that the Rouse model predicts $\lambda \propto M^2$. The previous disparity in the scaling behavior might, at least in part, be ascribed to the difficulty in precisely locating the onset of viscosity thinning in the second method. For convenience, however, later, we utilize the polymer relaxation times retrieved from the viscosity curves to make the shear rate a reduced variable.

Figures 7–10 show the resulting viscosity curves, all in reduced form ($\eta_{p,0}$ denotes the corresponding low-shear polymer viscosity). In general, time–temperature superposition applies excellently, except for the PS4 solution, as noted earlier. This essential feature implies that a moderate temperature variation or the effect of EV, in general, has little effect on the shape of the steady-state viscosity curve. Besides, the ability to superpose also indicates that the finite polymer concentrations investigated here should have little impact on the qualitative feature of the viscosity curve. On the other hand, the distinct behavior observed for the PS4 solution at high shear rates is somewhat perplexing, since the polymer molecular weight of PS4 differs from PS3 merely by a factor about 2 and, in particular, the solution exhibits no noticeable variation in the apparent solvent quality (see, for example,
Fig. 1 or Fig. 6). Specifically, the failure for the viscosity curves of PS4 to superpose may be better perceived from the original plot in Figure 5, where it is evident that the separation between the onset of viscosity thinning and the subsequent flattening reduces with increased temperature. To ensure that the aforementioned feature for PS4 solution is indeed universal for dilute high-molecular-weight PS solutions, we have additionally examined the results for another PS solution with a slightly larger molecular weight (i.e., $M_w = 2.9 \times 10^6$ Daltons, Fluka) and $c = 0.05$ wt % as functions of shear rate at four different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 11. Steady-state polymer viscosity for a PS solution with $M_w = 2.9 \times 10^6$ Daltons (PDI = 1.30; Fluka) and $c = 0.05$ wt % as functions of shear rate at four different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which the effect of EV or, more generally, segmental interactions has typically been omitted or greatly simplified, appear to be unable to quantitatively describe the experimental data on dilute PS solutions. For instance, it might well be that the apparent effect of EV, customarily incorporated in a molecular theory or simulation only indirectly through a couple of molecular parameters determined at equilibrium or at low flow rates, fails to fully account for the impact of segmental interactions on the flow behavior at high shear rates.

Recall also that time–temperature superposition of the viscometric properties typically applies on the occasion that a temperature-dependent polymer relaxation time has a predominant effect on the fundamental chain dynamics and thus the essential viscometric responses. For instance, this is usually the case with concentrated polymer systems in which the effects of HI and EV are generally unimportant (let alone their temperature dependences), or for dilute solutions with moderate polymer molecular weights at which the impact of the aforementioned mechanisms remains moderate, as suggested earlier. By contrast, for dilute solutions consisting of high-molecular-weight polymer solutes, it is possible that a moderate change in the system temperature suffices to considerably modify both the polymer relaxation time and, in particular, the detailed segmental interactions. Specifically, if the onset of a viscosity flattening observed in Figure 5 or Figure 11 at different temperatures corresponds roughly to the same degree of chain stretching, it might be that an increased temperature, despite having no evident effect on the apparent solvent quality, considerably reduces the segmental attractions and thus makes it easier for the polymer coil to stretch with external flows. On the other hand, the possibility of structure formation or intermolecular interactions cannot be excluded. Nevertheless, Brownian dynamics simulations of bead-spring models that can selectively and more faithfully reproduce the effects of HI, EV, chain extensibility, and even segmental attraction should help to clarify the current experimental phenomena.

Finally, in Figure 12, we compare the viscosity curves at a $\theta$-temperature for various polymer molecular weights. Disparity in the power-law indices is quite evident, and only the sample solution with the highest polymer molecular weight, PS4, exhibits a power-law index in close
agreement with the prediction of kinetic theory models considering finite chain extensibility, that is 0.68. Specifically, as the polymer molecular weight increases, the power-law index approaches from above to the previous asymptotic value. Note, in particular, that similar features have been reported for the steady-state intrinsic viscosity curves of monodisperse poly(α-methylstyrene) solutions under a good solvent condition, using a capillary rheometry, suggesting that the viscometric features currently revealed for the PS/DOP solutions could be typical of dilute polymer solutions. Overall, the data suggest that the effect of HI, in general, governs the power-law behavior of the steady-state polymer viscosity. As the polymer molecular weight becomes sufficiently large, however, the effect of finite chain extensibility eventually dominates, and the effects of system temperature are further complicated at high shear rates.

CONCLUSIONS

We reported viscometric data collected in a Couette rheometry on single-solvent, nonoverlapping PS/DOP solutions over a variety of temperatures and polymer molecular weights. The current data, largely consistent with early intrinsic viscometric data obtained in capillary rheometry system, suggest that both the high-shear and the low-shear viscometric properties of dilute polymer solutions are, in general, susceptible to the effect of HI, especially in view of the shape of the steady-state viscosity curve. Moreover, finite chain extensibility becomes dominant only at sufficiently high polymer molecular weights and shear rates. In particular, without noticeable variations in the apparent solvent quality, as evaluated on the basis of intrinsic viscosity data, the effect of temperature on the viscosity curve becomes exceptionally prominent at sufficiently high polymer molecular weights and shear rates. In this case, non-Newtonian responses other than a simple shear thinning in the steady-state viscometric properties become observable, and, in particular, time–temperature superposition ceases to apply since then. This essential finding suggests that, in addition to a temperature-dependent polymer relaxation time and apparent solvent quality, there remain unidentified mechanisms through which the system temperature may further complicate the high-shear viscometric responses in dilute high-molecular-weight polymer solutions.

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REFERENCES AND NOTES