Molecular Weight Dependence of the Viscosity of Highly Entangled Polyisobutylene

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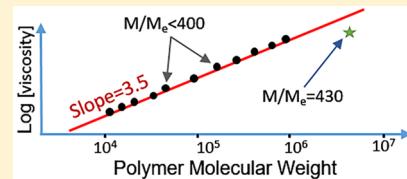[‡]American Society for Engineering Education, Washington, D.C. 20036-2479, United States
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Ⓢ *Supporting Information*

ABSTRACT: An unsolved problem in the viscoelastic properties of entangled linear polymers is the viscosity−molecular weight relationship. Experiments indicate a power law, $\eta_0 \propto M^a$, with $a = 3.5 \pm 0.2$, whereas the theoretical prediction for "pure reptation" is an exponent equal to 3.0. This discrepancy is ascribed to dynamic modes that compete with reptation so that a cubic dependence on M is observed only at sufficiently high molecular weights. That is, almost all existing experimental data are for polymers with too few entanglements to exhibit $\eta_0 \propto M^3$. To address this issue, we

carried out experiments on polyisobutylene having as many as 430 entanglements per chain. Because reentanglement of polymer melts prepared from solution takes extraordinarily long times (another unsolved problem in rheology), annealing was carried out for 5 years prior to the viscosity measurements. We determined that at all temperatures, η_0 was less than the extrapolation assuming the $M^{3.5}$ dependence of lower molecular weight polyisobutylene. This result is consistent with the idea that only at sufficiently high degrees of entanglement is pure reptation the operative mechanism, whereby linear flexible-chain polymers exhibit the predicted behavior. Our work is in good agreement with an earlier study on polybutadiene [Colby, R. H.; Fetters, L. J.; Graessley, W. W. Melt viscosity-molecular weight relationship for linear polymers. *Macromolecules* **1987**, *20*, 2226−2237.].

■ INTRODUCTION

An extant issue concerning the dynamics of well-entangled, linear polymers is the variation of their steady-state, zero-shear viscosity, η_0, with molecular weight. A plethora of experimental data indicate power-law behavior, $\eta_0 \propto M^a$, with an exponent a = 3.3−3.7.[1−5] The value of the exponent is at odds with the prediction of the tube model of polymer reptation, $a = 3.0$.[6] An exponent significantly larger than three poses an additional difficulty: M dependences of the time scales for diffusion and stress relaxation would be different, even though the two processes involve the same chain motions.[7−10] An explanation for the failure of the tube model is that dynamic modes compete with reptation, causing the observed power-law exponent to be larger than the predicted value.[4] These modes might include contour length fluctuations,[11,12] transverse motions allowing leakage between entanglements,[13] or excluded volume interactions.[14] Excepting the last, these ideas lead to the expectation that a would approach the asymptotic limit of 3.0 only at very high molecular weights, corresponding to perhaps 200 entanglements per chain.[8] Unidad et al.[15] suggested this limit would be reached sooner for polymer chains having larger packing lengths. In any case, it seems that virtually all existing experimental data are for polymers below the limiting high molecular weight required for the rheology to be dominated by reptation.

To address this issue, we measured the terminal dynamics of polyisobutylene (PIB), a material that has played a preeminent role in the development of polymer rheology. In the early 1950s, Robert Marvin distributed a PIB sample, known as "NBS-PIB", to laboratories throughout the world, allowing different measurement techniques to be brought to bear on a common material.[16] The resulting data were instrumental in the acceptance of the time−temperature superposition principle,[17] and PIB has been called the "most thermorheologically simple of all linear amorphous polymers".[18] This is ironic because the dynamic mechanical loss tangent of PIB exhibits a spectacular breakdown of $t−T$ superpositioning.[19] Indeed, PIB exhibits a number of interesting viscoelastic "anomalies".[20]

An advantage of PIB for studying the low-frequency dynamics is its stability. The polymer is fully saturated and cannot be cross-linked by any means, including ionizing radiation.[21] It is unusually resistant to thermal oxidative degradation. We illustrated this previously by measuring the rheological properties of NBS-PIB after more than 50 years storage at ambient conditions, with the results in good

agreement with those reported originally for the same sample.[19]

Herein, we measured the zero-shear viscosity of three PIBs, including a fractionated sample for which $M_w = 4.5 \times 10^6$ Da. This corresponds to 430 entanglements per chain ($M_e = 10\,500$ Da for PIB[22]), 4-fold higher than the existing data. Our results deviate from the measurements on lower molecular PIB, including literature data,[23] when extrapolated assuming an $M^{3.5}$ dependence. Errors herein due to uncertainties in either M (due to degradation) or η_0 (due to failure to attain steady state) are too small to accommodate an $M^{3.5}$ dependence. Thus, the limiting value of the M dependence of the viscosity of entangled PIB is in accord with the idea that other dynamic modes contribute to the terminal dynamics, whereby observation of the dependence predicted by the tube model for pure reptation requires unusually high molecular weights.

■ EXPERIMENTAL SECTION

PIBs from Sigma-Aldrich and American Polymer Standards were used as received, and a noncommercial sample from BASF was fractionated to reduce its polydispersity. The fractionation involved dissolution in cyclohexane by refluxing for several days, with the obtained solution then selectively precipitated by dropwise addition of acetone until the initial appearance of turbidity. After allowing the solution to settle overnight, any insoluble polymer was removed by filtering. The procedure was repeated over a couple of weeks, until no further cloudiness could be induced by the acetone addition. Several fractions were collected in this manner. Only the lowest M_w fraction was used because the others had molecular weights exceeding the resolution of the available SEC/light scattering instrumentation. This fraction was annealed for 1.6×10^8 s at ambient temperature prior to viscosity measurements for reasons discussed below.

Molecular weights (Table 1) were determined by SEC, the instrument consisting of a Waters 515 HPLC pump, Waters 2487

Table 1. Molecular Weights of PIBs

source	M_n (Da)	M_w (Da)	M_z (Da)	M_w/M_e
American Polymer Standards	1.64×10^5	3.02×10^5	5.21×10^5	29
Sigma-Aldrich	6.22×10^5	1.26×10^6	1.77×10^6	120
BASF (fractionated)	9.84×10^5	4.50×10^6	6.66×10^6	430

dual absorbance UV detector, Wyatt OPTILAB DSP interferometric refractometer, Wyatt DAWN EOS multi-angle light scattering detector, Wyatt ViscoStar viscometer, Wyatt QELS quasi-elastic light scattering instrument, Waters 717 plus autosampler, and 6 Styragel columns (HR6, HR5, HR4, HR3, HR1, and H0.5). Details of the measurement can be found in the Supporting Information, including the SEC trace for the highest M_w sample that affirms the absence of a high-molecular-weight tail.

The rheology was characterized using both Anton-Paar MCR 502 and 702 rheometers, with measurements repeated to ensure their reproducibility. Dynamic mechanical experiments at frequencies over the range $0.01 \le \omega$ (rad/s) ≤ 100 were carried out at temperatures over the range from −60 (for the highest M sample) to 217 °C. Transient, constant stress measurements were used to obtain the steady-state shear viscosity at temperatures from 100 to 217 °C. A procedure originally suggested by Leaderman[24] was utilized to efficiently attain steady-state conditions, while minimizing thermal degradation of the material. Thus, after application of the torsional stress (200 Pa), creep was measured for 200 000 s at 160 °C. The temperature was then increased to 180 °C for 10 000 s, followed by a return to 160 °C to obtain η_0. This procedure was repeated thrice to confirm the reproducibility of the steady-state measurements. Next, the temperature was decreased to 100 °C for 25 000 s, increased to 217 °C for 4000 s, and finally lowered to 160 °C. The last

measurement was used to assess the effect of thermal degradation, which caused a decrease of η_0 not exceeding 7%. Note that the test specimen was in a nitrogen atmosphere during the course of these measurements.

Viscosities obtained directly from steady-state creep were corroborated by measuring the creep recovery. After 350 100 s (~3.5 days) creep at 500 Pa stress at $T = 160$ °C, the stress was removed, and the sample was allowed to recover for 350 100 s. The recovered strain was subtracted from the creep strain to yield a value for the viscosity. We also employed an approximation method[25] applicable to flow prior to attainment of steady state. These results can be found in the Supporting Information.

■ RESULTS

Dynamic mechanical data were obtained as a function of frequency for temperatures up to 217 °C, from which the master curves in Figure 1 were constructed. In the inset, the
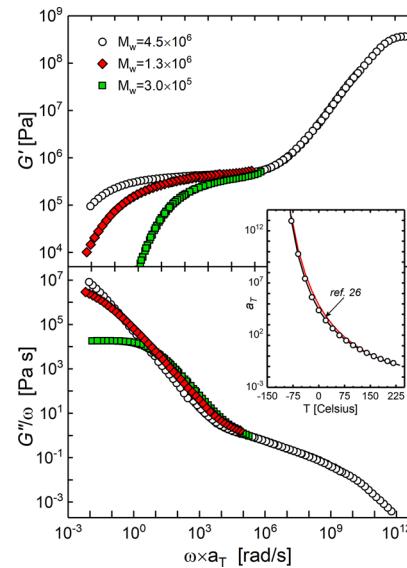

Figure 1. Master curves of the storage modulus and dynamic viscosity at a reference temperature of 160 °C. The inset displays the time–temperature shift factors (symbols), along with lines representing the fit of eq 1 and the literature result.[26]

shift factors, a_T, determined from superposing the loss tangent to avoid vertical shifts are compared to literature data.[26] The agreement is satisfactory, although in the glass-transition region ($T_g = -71$ °C for PIB[27]), the time–temperature superposition principle breaks down[19] and the shift factors are approximate. The data were described by the Vogel–Fulcher equation

$$a_T = a_{T,\infty}\exp\left(\frac{B}{T - T_0}\right)$$

(1)

with values for the material constants listed in Table 2.

Table 2. Fit Parameters (Eq 1) for PIB ($M_w = 4.50 \times 10^6$ Da)

property	T range (°C)	$a_{T,\infty}$, $\eta_{T,\infty}$	B (K)	T_0 (K)
loss tangent[a]	−60 to 217	2.64×10^{-5}	3176	115.5
η_0 (Pa s)	100−217	2607 Pa s	3176	115.5

[a]Reference temperature = 160 °C.

At lower frequencies, the master curve of the storage modulus reveals a rubbery plateau that for the highest molecular weight PIB encompasses ~8.7 decades of reduced frequency (determined from the crossing points where the loss tangent is unity). For a scaling exponent between 3 and 3.4, the plateau for the lowest M_w PIB would then span between 4.7 and 5.2 decades. The G' plateau in Figure 1 is about 5.3 decades, roughly consistent with an exponent = 3. The master curve for the dynamic viscosity, η', in Figure 1 remains non-Newtonian at a reduced frequency of ~10^{-3} rad/s at the reference temperature (160 °C). Thus, measuring the dynamics at frequencies low enough to observe terminal behavior requires transient experiments.

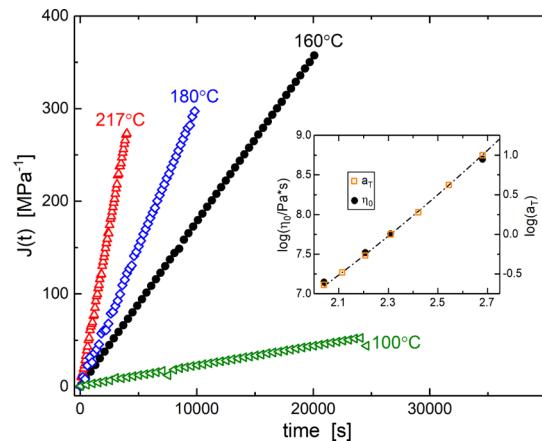Figure 2 displays the creep compliance for various temperatures, with steady-state flow indicated by a constant
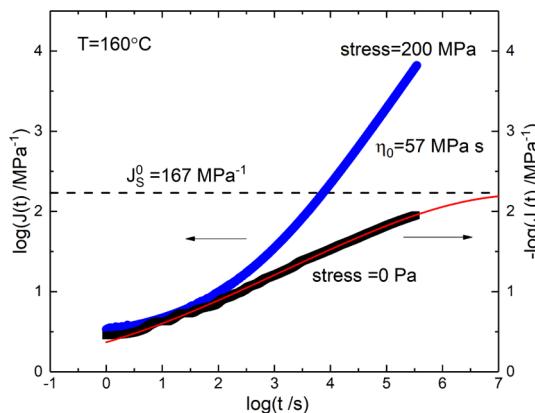

Figure 3. Compliance during constant stress creep (upper curve) and stress-free recovery (lower curve). The solid line to $J_r(t)$ is the fit of eq 2, with the stretch exponent = 0.36 and the indicated value of the steady-state recoverable compliance.

stretched exponential function applied to the terminal dispersion of entangled polymers has a long history,[28] with a value of $\beta = 0.57$ derived from a model for monodisperse polymers.[29,30] This is consistent with the smaller stretch exponent for our sample, which has some polydispersity. After subtraction of the measured recoverable compliance, $J_S^0 = 167$ MPa^{-1}, the slope of the compliance gave $\eta_0 = 57$ MPa s (Figure 3), in agreement with the terminal value of the inverse slope of the creep curve.

If the creep data in Figures 2 and 3 did not correspond to steady state, the zero-shear viscosity would be underestimated. To confirm that this potential error was not significant, we employed the approximation method of Ninomiya.[25] This analysis, detailed in the Supporting Information, yielded $\eta_0 = 57 \pm 1$ MPa s, confirming the accuracy of the above results.

■ DISCUSSION

Figure 4 shows the results of PIB at three temperatures (η_0 for all temperatures are in Table 3), along with the literature

Figure 2. Creep compliance measured initially at 160 °C (circles) and following jumps to the indicated temperatures. Once steady state is attained, it persists at all subsequent temperatures. The inset shows the viscosities from the inverse slopes of the creep data, along with the fit of eq 1, as well as the shift factors for the master curve of the dynamic mechanical data in Figure 1.

slope d$J(t)$/dt. At 160 °C, this required almost 2.5 days at a total shear strain on the order of 0.8. To minimize the duration of the experiments, the temperature jump method[24] was applied as described in the Experimental Section. The temperature dependence of η_0, obtained as the reciprocal slope at steady state, was well-described by the Vogel–Fulcher equation (Table 2). The equivalence of the T dependences of the shift factors (a dynamic measurement) and the viscosities (transient measurement) corroborate the accuracy of the latter because η_0 depends on the accuracy of the torque and displacement measurements, whereas determination of a_T does not.

To check the creep result, at 160 °C the stress was removed and the recovery of the PIB was measured for 350 100 s (4 days). The instrumental resolution was inadequate to follow the complete recovery, so the recoverable compliance data were fit using[1]

$$J_r(t) = J_g + (J_S^0 - J_g)\left(1 - \exp\left(-\left[\frac{t}{\tau}\right]^{\beta}\right)\right)$$

(2)

in which J_S^0, τ, and β are material constants. Ostensibly the glassy compliance, J_g actually reflects instrumental effects. The results are shown in Figure 3, with the best-fit values $J_g = 1$ MPa^{-1}, $J_S^0 = 167$ MPa^{-1}, $\beta = 0.36$, and $\tau = 690\,000$ s. A
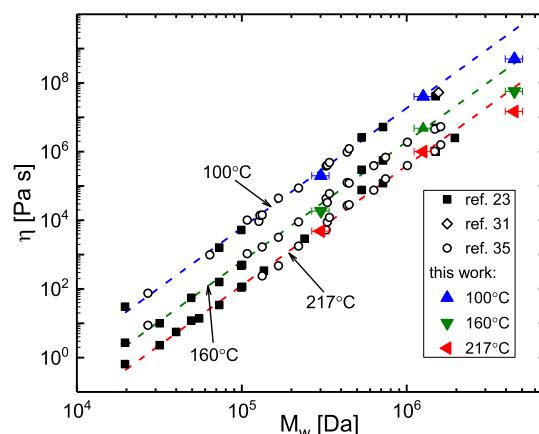

Figure 4. Zero-shear viscosity as a function of molecular weight at three temperatures. The data from ref 23 were corrected for shear rate dependence,[34] and the molecular weights from the intrinsic viscosity were converted to M_w using the procedure in ref 35. The lines are power-law fits to literature data for $M_w < 2 \times 10^6$ Da, yielding $\eta_0 \approx M^{3.49\pm0.06}$. The new results (triangles) deviate for the highest M_w from the extrapolated lines. The uncertainty M_w, due primarily to potential effects of polydispersity, is indicated.

Table 3. Zero-Shear Viscosities (MPa s) of PIB

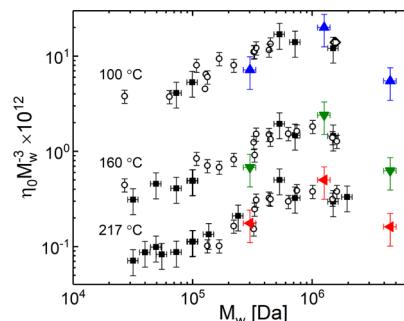| T [°C]	M_w (Da)		
	3.02×10^5	1.26×10^6	4.50×10^6
100	$1.97 \times 10^{-1} \pm 0.002$	39.8 ± 0.5	500 ± 20
160	$1.81 \times 10^{-2} \pm 3 \times 10^{-4}$	4.53 ± 0.02	57 ± 1
180			33 ± 1
217	$4.83 \times 10^{-3} \pm 2 \times 10^{-5}$	1.15 ± 0.05	14 ± 0.5

Figure 5. Zero-shear viscosity normalized by the cubic power of molecular weight at the three indicated temperatures (symbols as in Figure 4).

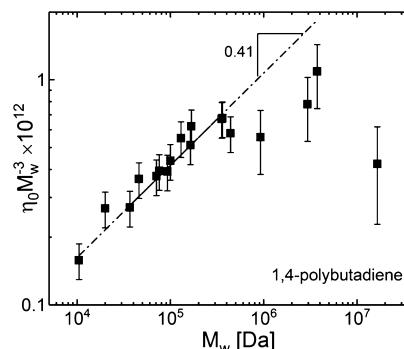**Figure 6.** Zero-shear viscosity normalized by the cubic power of molecular weight for polybutadiene.[8]

data.[23,31−35] The latter exhibit $\eta_0 \approx M^{3.5}$ behavior, whereas at all temperatures the highest M PIB herein exhibits a weaker dependence on molecular weight, in better accord with tube models describing pure reptation.[6] While polydispersity of the sample herein and of those reported in the literature for PIB introduces some uncertainty,[36] this is minimized by the use of the weight-average value.[1,37,38] Using proposed corrections for the effect of polydispersity[39−41] changes the data in Figure 4 by about 12%, an insignificant amount on an ordinate scale encompassing 9 decades.

The explanation for a molecular weight dependence stronger than cubic is that mechanisms other than reptation contribute to the terminal dynamics of entangled polymers.[11−14] This hypothesis requires experimental verification; however, such tests are almost nonexistent because of the experimental difficulties. Colby et al.[8] reported a departure from $\eta_0 \approx M^{3.4}$ for polybutadiene having more than 8000 entanglements per chain, the data roughly consistent with an asymptotic M^3 at sufficiently high M. Steady state was not attained in the creep viscosities measured in that work, requiring utilization of the Ninomiya approximation method.[25] Moreover, at short times, the creep compliance was observed to decrease over time,[8] suggesting the possibility that the polymer had not reached equilibrium (incomplete reentanglement) after recovery from solution. This would make the measured steady-state viscosity artifactually low. Note that the time for the recovery of entanglements can be as much as 2 orders of magnitude longer than the linear relaxation time.[42−45]

A crossover to asymptotic M^3 behavior has been reported for polyisoprene from viscosity measurements[15] and dielectric spectroscopy,[46] onsetting at $M_w \approx 2.5 \times 10^5$ and 8.4×10^4 Da, respectively. However, in neither case was the limiting behavior clearly evident (see Supporting Information), and using unsaturated polymers for measurements at very high temperatures entails the rise of significant thermal degradation.

For PIB, reentanglement times have been measured that are ∼60 times greater than the linear relaxation time.[45] In order to ensure a completely equilibrated material in the present work, prior to the viscosity measurements the fractionated sample was annealed at room temperature for 5 years, 1000-fold longer than the terminal relaxation time. Our observation of viscosities that are significantly lower than an extrapolation assuming a 3.5 power law thus corroborates the interpretation of the behavior observed for polybutadiene—the dependence on the molecular weight of the viscosity becomes weaker for sufficiently entangled polymers.

As shown by Colby et al.,[8] plotting the viscosity normalized by M^3 removes most of the molecular weight dependence, facilitating observation of any deviation from the power law seen at lower M_w. As seen in Figure 5, displaying $\eta_0/M_w{}^3$ for the three highest temperatures, departure from $\eta_0 \propto M^{3.5}$ is readily apparent for $M_w > 10^6$ Da. The behavior of our data in Figure 5 is very similar to the prior results for polybutadiene (Figure 6),[8] including an apparent weak maximum in $\eta_0/M3$;

however, in both cases, the data are too sparse to be definitive about the exact behavior. Nor can we verify the anticipated cubic dependence because of the limited span of the PIB viscosity data. There is no statistical support for even the assumption of power-law behavior for results spanning less than 2 decades on either axis.[47] We are limited to concluding that for well-entangled PIB (>400 entanglements per chain), the dependence of the viscosity on molecular weight is weaker than the power law seen at lower M.

■ CONCLUSIONS

The tube model of the rheology of entangled polymers makes some predictions that deviate from experimental results, for example, the shape of the terminal dispersion[6,48] and the temperature dependence of the terminal dynamics.[19,22,49] The focus herein is the well-known deviation of the viscosity from the predicted cubic power-law dependence on M, attributed to other processes competing with pure reptation. We find here that for PIB having more than ca. 200 entanglements per chain, the contribution from these other mechanisms is diminished, consistent with a previous study of high M polybutadiene.[8] Accordingly, the M dependence becomes closer to that of the time scale for diffusion[7,8] and to the prediction for pure reptation;[6] however, the present data are inadequate to serve as verification of an M^3 dependence.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00993.

SEC of PIB; Ninomiya approximation; and polyisoprene data (PDF)

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Notes
The authors declare no competing financial interest.

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