Molecular Weight Dependence of the Viscosity of Highly Entangled Polyisobutylene

T. C. Ransom,[*,†] D. Roy,[†,‡] J. E. Puskas,[¶] G. Kaszas,[§] and C. M. Roland[*,†]

†*Chemistry Division, Naval Research Laboratory, Washington, DC 20375*
‡*US Patent and Trademark Office, Alexandria, VA 22314*
¶*The Ohio State University, Dept. Food, Agricultural, and Biological Eng., Wooster, OH 44691*
§*PolyFiberMatrix LLC, Akron, OH 44325*

E-mail: timothy.ransom.ctr@nrl.navy.mil; mike.roland@nrl.navy.mil

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 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 430 entanglements per chain. Since reentanglement of polymer melts prepared from solution takes extraordinarily long times (another unsolved problem in rheology), annealing was carried out for five 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 the 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 timescales for diffusion and stress relaxation would be different, even though the two processes involve the same chain motions.[7,8] 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,[9,10] transverse motions allowing leakage between entanglements,[11] or excluded volume interactions.[12] 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] This implies 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 polyisobutylene sample, known as "NBS-PIB", to laboratories throughout the world, allowing different measurement techniques to be brought to bear on a common material.[13] The resulting data were instrumental in the acceptance of the time-temperature superposition principle,[14] and PIB has been called the "most thermorheologically simple of all linear amorphous polymers".[15] This is ironic since the dynamic mechanical loss tangent of PIB exhibits a spectacular breakdown of t-T superpositioning.[16] Indeed, PIB exhibits a number of interesting viscoelastic "anomalies".[17]

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.[18] 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.[16]

In this work we measured the zero-shear viscosity of three polyisobutylenes, including a fractionated for which $M_w = 4.5 \times 10^6$ Da. This corresponds to 430 entanglements per chain ($M_e = 10,500$ Da for PIB[19]), fourfold higher than existing data. Our results deviate from the measurements on lower molecular weight PIB, including literature data,[20] 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 polyisobutylene 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

Polyisobutylenes from Sigma-Aldrich and American Polymer Standards were used as received, and a non-commercial 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, since the others had molecular weights exceeding the resolution of the available SEC 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 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 $0.01 \leq \omega$ (rad/s) ≤ 100 were carried out at temperatures over the range from -60 (for the highest M sample) to 217 °C. Transient, constant stress

Table 1: Molecular weights of polyisobutylenes

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	14.50×10^6	6.66×10^6	430

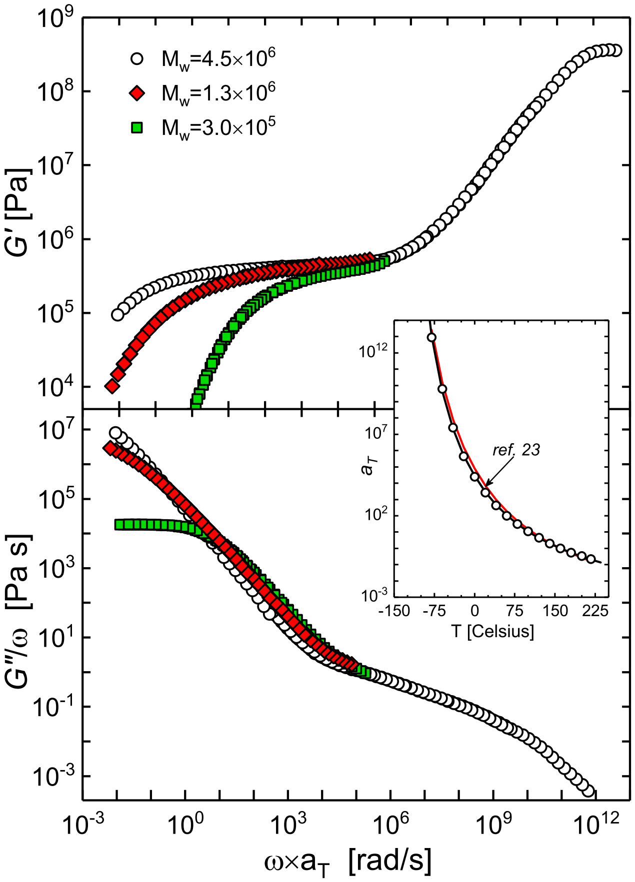

Figure 1: Master curves of the storage modulus and dynamic viscosity at a reference temperature of 160 °C. The inset displays the time-temperature shift factors (symbols), along with lines representing the fit of eq. 1 and the literature result.[22]

measurements were used to obtain the steady-state shear viscosity at temperatures from 100 to 217 °C. A procedure originally suggested by Leaderman[21] 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 4,000 s, and finally lowered to 160 °C. The last measurement at 160 °C was used to assess the effect of thermal degradation, which caused a decrease of η_0 not exceeding 7%. Note 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 350,000 s creep at 500 Pa at T = 160 °C, the stress was removed and the sample allowed to recover for 350,000 s. The recovered strain was subtracted from the creep strain to yield a value for the viscosity. We also employed an approximation method[23] 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 shift factors, a_T, determined from superposing the loss tangent to avoid vertical shifts, are compared to literature data.[22] The agreement is satisfactory, although in the glass transition region ($T_g = -71\,°\mathrm{C}$ for PIB),[24] the time-temperature superposition principle breaks down[16] and the shift factors are approximate. The data were described by the Vogel-Fulcher equation

$$a_T = a_{T,\infty} \exp\left(\frac{B}{T - T_0}\right) \tag{1}$$

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)	$a_{T,\infty}$	B (K)	T_0 (K)
loss tangent*	-60 to 217	2.74×10^{-5}	3,400	109.2
η_0 (Pa s)	100 to 217	6.79×10^3 (Pa s)	$2,800 \pm 20$	123 ± 1

*reference $T = 160\,°\mathrm{C}$

At lower frequencies the master curve of the storage modulus reveals a rubbery plateau that for the highest molecular weight PIB encompasses more than five decades of reduced frequency. If the terminal relaxation time scales as M^3, the plateau for the intermediate M_w PIB would span almost 4 decades. However, since G' is not strictly independent of frequency in this region, accurately quantifying the extent of the plateau is problematic. The master curve for the dynamic viscosity, η', in Fig. 1 remains non-Newtonian, at a reduced frequency of $\sim 10^{-3}$ rad/s at the reference temperature (160 °C). Thus, measuring the dynamics at frequencies low enough to observe terminal behavior requires transient experiments.

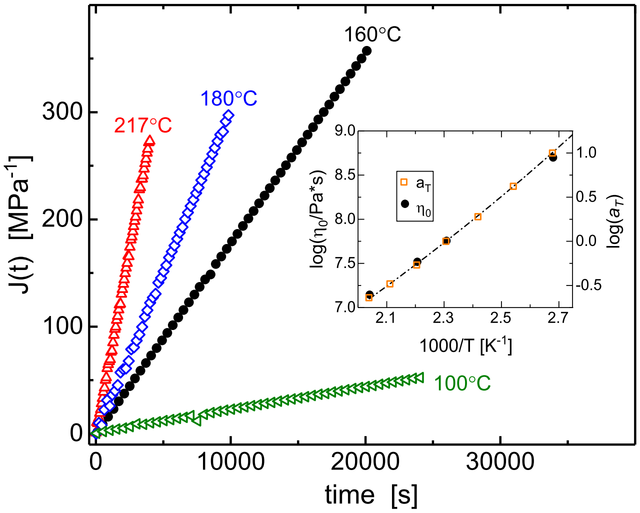

Figure 2: Creep compliance measured initially at 160 °C (circles) and following jumps to the indicated temperatures. Once steady state is attained, it persists at all subsequent temperatures. The inset shows the viscosities from the inverse slopes of the creep data, along with the fit of eq. 1, as well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

Figure 2 displays the creep compliance for various temperatures, with steady-state flow indicated by a constant slope $dJ(t)/dt$. 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[21] 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) corroborates the accuracy of the latter, since η_0 depend 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 measured for 350,100 s (four days). The instrumental resolution was inadequate to follow the complete recovery, so the recoverable compliance data were fit using[1]

$$J_r(t) = J_g + (J_S^0 - J_g)\left(1 - \exp\left(-\left[\frac{t}{\tau}\right]^{\beta}\right)\right) \quad (2)$$

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 $J_g = 1\,\mathrm{MPa}^{-1}$, $J_s^0 = 167\,\mathrm{MPa}^{-1}$, $\beta = 0.36$, and $\tau = 690,000\,\mathrm{s}$. A stretched exponential function applied to the terminal dispersion of entangled polymers has a long history,[25] with a value of 0.57 derived from a model for monodisperse polymers.[26,27] This is consistent with the smaller stretch exponent for our sample, which has some polydispersity. After subtraction of the measured recoverable compliance, $J_S^0 = 167\,\mathrm{MPa}^{-1}$, the slope of the compliance gave

$\eta_0 = 54$ MPa s (Fig. 3), in agreement with the long-time value of the inverse slope of the creep curve.

If the creep data in Figs. 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 due to Ninomiya.[23] This analysis, detailed in the Supporting Information, yielded $\eta_0 = 57 \pm 1$ MPa s, confirming the accuracy of the above results.

Discussion

In Figure 4 are collected our results for PIB at three temperatures (η_0 for all temperatures are in Table 3), along with the literature data.[20,28–32] The latter exhibit $\eta_0 \sim M^{3.5}$ behavior, whereas at all temperatures the highest M PIB herein exhibits a weaker dependence on molecular weight, which is 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,[33] this is minimized by the use of the weight-average value.[1,34,35] Using proposed corrections for the effect of polydispersity[36,37] changes the data in Fig. 4 by about 12%, an insignificant amount on an ordinate scale encompassing more than nine 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.[9–12] This hypothesis requires experimental verification; however, such tests are almost nonexistent due to the experimental difficulties. Colby et al.[8] reported a departure from $\eta_0 \sim M^{3.4}$ for polybutadiene having more than 8,000 entanglements per chain, the data roughly consistent with an asymptotic M^3 at sufficiently high M. The viscosity in that work was measured by creep utilizing the Ninomiya approximation method.[23] However, at short times the creep compliance was observed to decrease over time,[8] suggesting the possibility that the polymer had not reached equilibrium (was not completely reentangled) after recovery from solution. This would make the measured steady-state viscosity artificially low. Note that the time for recovery of entanglements can be as much as two orders of magnitude longer than the linear relaxation time.[38–40] This uncertainty tempers acceptance of the polybutadiene work.

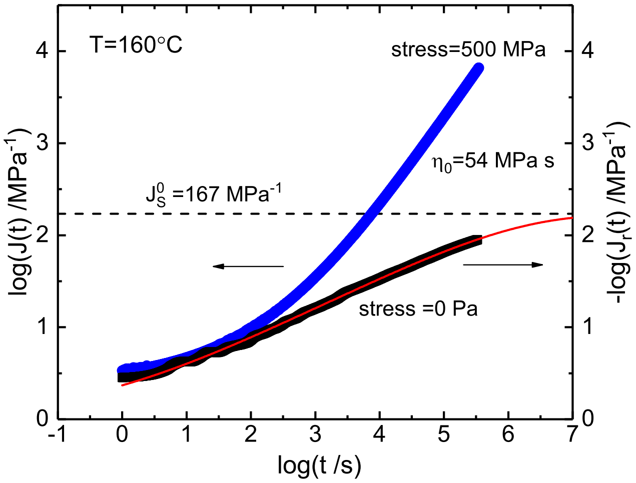

Figure 3: Compliance during constant stress creep (upper curve) and stress-free recovery (lower curve). The solid line to $J_r(t)$ is the fit of eq. 2, with the stretch exponent =0.36 and the indicated value of the steady-state recoverable compliance

For PIB, reentanglement times have been measured that are $\sim$ 60 times greater than the linear relaxation time.[41] In order to ensure a completely equilibrated material in the present work, prior to the viscosity measurements the fractionated sample was annealed at RT for 5 years, a thousandfold 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 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 th power-law seen at lower M_w. As seen in Figure 5, displaying η_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

Table 3: Zero-shear viscosities (MPa s) of PIB samples (uncertainties 5–10%)

M_w (MDa)	100 °C	160 °C	180 °C	217 °C
0.302	0.197	1.81×10^{-2}	—	4.83×10^{-3}
1.26	39.8	4.53	—	1.15
4.50	500	57	33.0	14.7

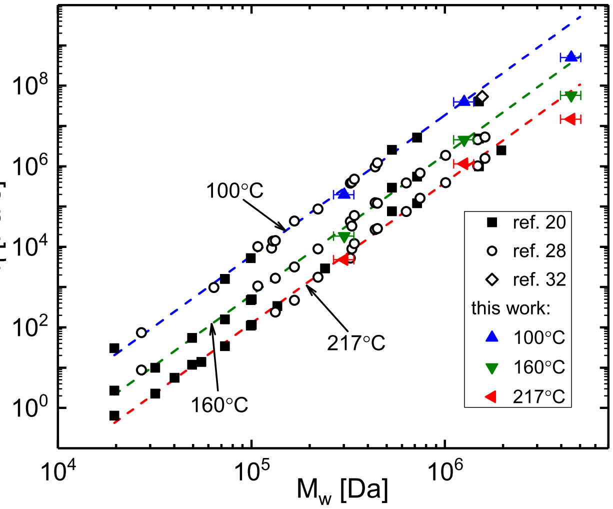

Figure 4: Zero-shear viscosity as a function of molecular weight at three temperatures. The data from ref. [20] were corrected for shear rate dependence[31] and the molecular weights from the intrinsic viscosity converted to M_w using the procedure in ref. [32]. The lines are power-law fits to literature data for $M_w < 2 \times 10^6$ Da, yielding $\eta_0 \sim M^{3.49\pm0.06}$. 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.

in Fig. 5 is very similar to the prior results for polybutadiene (Figure 6),[8] including an apparent weak maximum in η_0/M_w^3; 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 two decades on either axis.[42] 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.

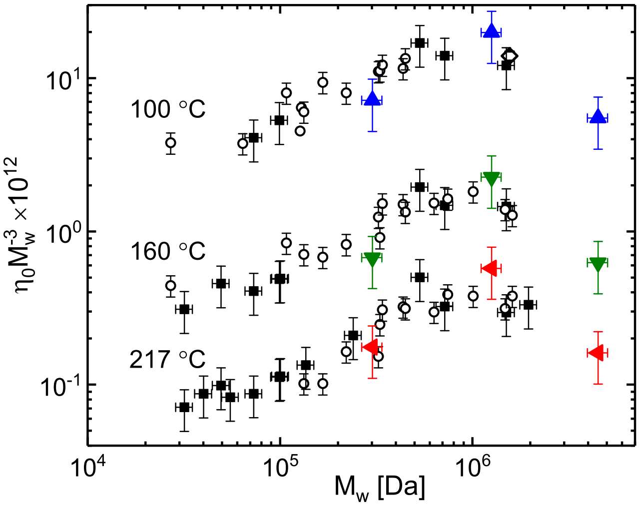

Figure 5: Zero-shear viscosity normalized by the cubic power of molecular weight at the three indicated temperatures (symbols as in Fig. 4).

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,[6,43] and the temperature dependence of the terminal dynamics.[15,19,44] The focus herein in the well-known deviation of the viscosity from the predicted cubic power-law dependence on M, attributed to processes other than reptation affecting the relaxation. 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.

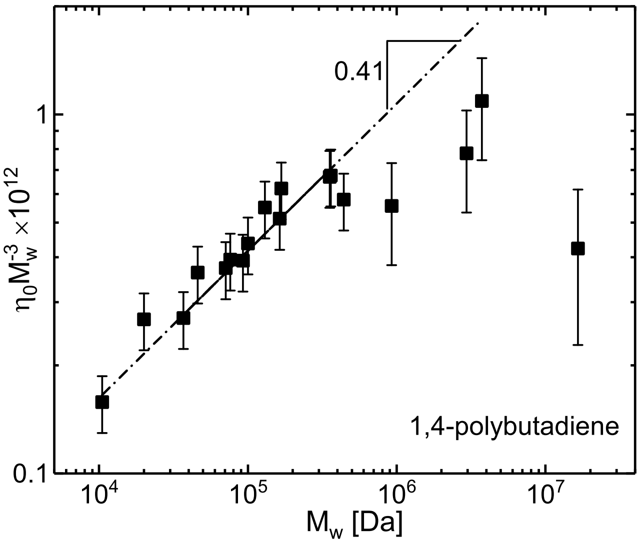

Figure 6: Zero-shear viscosity normalized by the cubic power of molecular weight for polybutadiene.[8]

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References

(1) Ferry, J. D. *Viscoelastic properties of polymers*; John Wiley & Sons, 1980.

(2) Lodge, T. P.; Rotstein, N. A.; Prager, S. Dynamics of entangled polymer liquids: Do linear chains reptate? *Adv. Chem. Phys.* **1992**, *79*, 1–132.

(3) McLeish, T. C. B. Tube theory of entangled polymer dynamics. *Adv. Phys.* **2002**, *51*, 1379–1527.

(4) Watanabe, H. Viscoelasticity and dynamics of entangled polymers. *Prog. Polym. Sci.* **1999**, *24*, 1253–1403.

(5) Berry, G. The viscosity of polymers and their concentrated solutions. *Adv. Polym. Sci.* **1968**, *5*, 261–357.

(6) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics Clarendon Press*; Clarendon Press: Oxford, 1986.

(7) Scher, H.; Shlesinger, M. F. On reptation in polymer melts. *J. Chem. Phys.* **1986**, *84*, 5922–5924.

(8) Colby, R. H.; Fetters, L. J.; Graessley, W. W. The melt viscosity-molecular weight relationship for linear polymers. *Macromolecules* **1987**, *20*, 2226–2237.

(9) Doi, M. Explanation for the 3.4-power law for viscosity of polymeric liquids on the basis of the tube model. *J. Polym. Sci. Polym. Phys. Ed.* **1983**, *21*, 667–684.

(10) Milner, S. T.; McLeish, T. C. B. Reptation and contour-length fluctuations in melts of linear polymers. *Phys. Rev. Lett.* **1998**, *81*, 725.

(11) Graessley, W. W. Some phenomenological consequences of the Doi–Edwards theory of viscoelasticity. *J. Polym. Sci. Polym. Phys. Ed.* **1980**, *18*, 27–34.

(12) Deutsch, J. M. The dynamics of entangled polymers. *J. Physique* **1987**, *48*, 141–150.

(13) Marvin, R. S. Proceedings of the Second International Congress on Rheology; Harrison, V. G. W., Ed. 1954; Butterworths: London.

(14) Ferry, J. D. Some reflections on the early development of polymer dynamics: Viscoelasticity, dielectric dispersion, and self-diffusion. *Macromolecules* **1991**, *24*, 5237–5245.

(15) Plazek, D. J. 1995 Bingham Medal Address: Oh, thermorheological simplicity, wherefore art thou? *J. Rheol.* **1996**, *40*, 987–1014.

(16) Plazek, D. J.; Chay, I.-C.; Ngai, K. L.; Roland, C. M. Viscoelastic properties of polymers. 4. Thermorheological complexity of the softening dispersion in polyisobutylene. *Macromolecules* **1995**, *28*, 6432–6436.

(17) Kunal, K.; Paluch, M.; Roland, C. M.; Puskas, J. E.; Chen, Y.; Sokolov, A. P.

Polyisobutylene: A most unusual polymer. *J. Polym. Sci. B: Polym. Phys.* **2008**, *46*, 1390–1399.

(18) Bohm, G. G. A.; Tveekrem, J. O. The radiation chemistry of elastomers and its industrial applications. *Rubber Chem. Technol.* **1982**, *55*, 575–668.

(19) Roland, C. M. *Viscoelastic behavior of rubbery materials*; Oxford University Press, 2011.

(20) Fox Jr, T. G.; Flory, P. J. Further studies on the melt viscosity of polyisobutylene. *J. Phys. Coll. Chem.* **1951**, *55*, 221.

(21) Leaderman, H.; Smith, R. G.; Jones, R. W. Rheology of polyisobutylene. II. Low molecular weight polymers. *J. Polym. Sci.* **1954**, *14*, 47–80.

(22) Sanders, J. F.; Ferry, J. D. Dynamic mechanical properties of cross-linked rubbers. VII. Butyl rubber networks. *Macromolecules* **1974**, *7*, 681–684.

(23) Ninomiya, K. An extrapolation method for estimating steady-flow viscosity and steady state compliance from creep data. *J. Phys. Chem.* **1963**, *67*, 1152–1152.

(24) McGrath, K. J.; Ngai, K. L.; Roland, C. M. Temperature dependence of segmental motion in polyisobutylene and poly (vinylethylene). *Macromolecules* **1992**, *25*, 4911–4914.

(25) Knoff, W. F.; Hopkins, I. L.; Tobolsky, A. V. Studies on the stress relaxation of polystyrenes in the rubbery flow region. II. *Macromolecules* **1971**, *4*, 750–754.

(26) McKenna, G. B.; Ngai, K. L.; Plazek, D. J. Differences in the molecular weight and the temperature dependences of self-diffusion and zero shear viscosity in linear polyethylene and hydrogenated polybutadiene. *Polymer* **1985**, *26*, 1651–1653.

(27) Santangelo, P. G.; Ngai, K. L.; Roland, C. M. The coupling model approach to the terminal relaxation. *Polymer* **1998**, *39*, 681–687.

(28) Ferry, J. D.; Grandine Jr, L. D.; Fitzgerald, E. R. The Relaxation Distribution Function of Polyisobutylene in the Transition from Rubber-Like to Glass-Like Behavior. *J. Appl. Phys.* **1953**, *24*, 911–916.

(29) Leaderman, H.; Smith, R. G.; Williams, L. C. Rheology of polyisobutylene. III. Elastic recovery, non-Newtonian flow, and molecular weight distribution. *J. Polym. Sci.* **1959**, *36*, 233–257.

(30) Fetters, L. J.; Lohse, D. J.; Milner, S. T.; Graessley, W. W. Packing length influence in linear polymer melts on the entanglement, critical, and reptation molecular weights. *Macromolecules* **1999**, *32*, 6847–6851.

(31) Krigbaum, W. R.; Flory, P. J. Molecular weight dependence of the intrinsic viscosity of polymer solutions. II. *J. Polym. Sci.* **1953**, *11*, 37–51.

(32) Fetters, L. J.; Graessley, W. W.; Kiss, A. D. Viscoelastic properties of polyisobutylene melts. *Macromolecules* **1991**, *24*, 3136–3141.

(33) Doi, M.; Edwards, S. F. Dynamics of concentrated polymer systems. Part 3.The constitutive equation. *J. Chem. Soc. Fara. Trans. 2: Molecular and Chemical Physics* **1978**, *74*, 1818–1832.

(34) Struglinski, M. J.; Graessley, W. W. Effects of polydispersity on the linear viscoelastic properties of entangled polymers. 1. Experimental observations for binary mixtures of linear polybutadiene. *Macromolecules* **1985**, *18*, 2630–2643.

(35) Roy, D.; Giller, C. B.; Hogan, T. E.; Roland, C. M. The rheology and gelation of bidisperse 1, 4-polybutadiene. *Polymer* **2015**, *81*, 111–118.

(36) Zeichner, G. R.; Patel, P. D. The influence of molecular-weight distribution on melt

rheology of polypropylene. J. Rheol. 1982; pp 93–93.

(37) Wasserman, S. H.; Graessley, W. W. Prediction of linear viscoelastic response for entangled polyolefin melts from molecular weight distribution. *Polym. Eng. Sci.* **1996**, *36*, 852–861.

(38) Robertson, C. G.; Warren, S.; Plazek, D. J.; Roland, C. M. Reentanglement kinetics in sheared polybutadiene solutions. *Macromolecules* **2004**, *37*, 10018–10022.

(39) Yamaguchi, M.; Gogos, C. G. Quantitative relation between shear history and rheological properties of LDPE. *Advances in Polymer Technology: Journal of the Polymer Processing Institute* **2001**, *20*, 261–269.

(40) Plazek, D. J.; Raghupathi, N.; O'rourke, V. M. New evidence for molecular entanglements. *J. Polym. Sci. Polym. Phys. Ed.* **1980**, *18*, 1837–1846.

(41) Roy, D.; Roland, C. M. Reentanglement kinetics in polyisobutylene. *Macromolecules* **2013**, *46*, 9403–9408.

(42) Stumpf, M. P. H.; Porter, M. A. Critical truths about power laws. *Science* **2012**, *335*, 665–666.

(43) Schroeder, M. J.; Roland, C. M. Normal mode relaxation of polyisoprene in blends with vinyl polybutadienes. *Macromolecules* **1999**, *32*, 2000–2003.

(44) Ngai, K. L.; Plazek, D. J. Identification of different modes of molecular motion in polymers that cause thermorheological complexity. *Rubber Chemistry and Technology* **1995**, *68*, 376–434.