Macromolecules 1992, 25, 7060–7062

Notes

Molecular Weight Dependence of the Critical Strain Rate for Flexible Polymer Solutions in Elongational Flow

Malika J. Menasveta and David A. Hoagland*

Department of Polymer Science and Engineering,
University of Massachusetts at Amherst,
Amherst, Massachusetts 01003

Received June 19, 1992
Revised Manuscript Received September 11, 1992

Introduction

The abrupt appearance of intense flow birefringence from dilute solutions of flexible polymers, noted in both stagnation-type[15] and transient[6] elongational flows, is an unambiguous manifestation of the ability of hydrodynamic forces to induce profound segmental rearrangements in isolated polymer coils. These rearrangements have often been explained in terms of the "coil–stretch" transition,[7] a sudden and drastic conformational rearrangement predicted when hydrodynamic drag initially overcomes Brownian forces that randomize polymer conformation in quiescent solution. Theories for the coil–stretch transition[7-9] suggest that hydrodynamic forces become dominant when the applied strain rate $\dot{\epsilon}$ exceeds a critical value $\dot{\epsilon}_c$. According to standard arguments, the reciprocal of the chain's longest relaxation time τ provides an estimate for $\dot{\epsilon}_c$, i.e.

$$\dot{\epsilon}_c = A/\tau \tag{1}$$

where A is an order unity constant. When $\dot{\epsilon}$ exceeds $\dot{\epsilon}_c$, the polymer coil will stretch and, if the flow is maintained for a sufficient period t, become highly deformed. Assuming that the deformation proceeds affinely with the surrounding fluid, the maximum coil extension equals the fluid strain $\dot{\epsilon}t$. Although not directly addressed in most theories, large segmental orientation—and thus flow birefringence—is an inevitable consequence of extreme changes in global chain conformation.

Two research groups[1,3-5] report that, irrespective of solvent quality

$$\dot{\epsilon}_c \sim N^{-1.5} \tag{2}$$

where N is the degree of polymerization. Two additional studies in good solvents[10,11] also note power law behavior but with a larger negative N exponent of approximately −1.8. For a non-free-draining coil under Θ conditions the exponent expected from eq 1 is −1.5, while the same equation predicts −1.8 when solvent conditions are good; these are the exponents derived from the Zimm model for τ when excluded-volume effects are added. Despite the obvious discrepancies between theory and experiment, and even between different experiments, one group employed eq 2 under good solvent conditions in a procedure for determining the molecular weight and the molecular weight distribution of fractured polymer chains.[12,13] To rationalize experimental observations for the N dependence of $\dot{\epsilon}_c$, Rabin et al. proposed two new polymer/flow models, one incorporating suppression of excluded volume in high strain rate flow[14] and the second postulating that the coil–stretch transition occurs at the stability limit of the coiled state.[15,16] The latter predicts a shift in the N exponent from −1.5 to −1.6 as the solvent quality improves from Θ conditions. Existing data sets are inadequate to fully test either of Rabbin's predictions.

In this paper we present a rigorous experimental verification of the N dependence of $\dot{\epsilon}_c$ where, for the first time, each parameter, $\dot{\epsilon}_c$ and N, is independently characterized. The polymers are monodisperse polystyrene, and the solvent is toluene at room temperature. Polymer molecular weights are determined from angular-dependent light scattering, and the critical strain rates are obtained via flow birefringence measurements. In all previous investigations, N was accepted as given by the commercial supplier, our experience has shown that such N values are often in substantial error, especially in the large N range of greatest interest. The N range over which the abrupt onset of flow birefringence can be observed is small, about 1 order of magnitude, so errors in N must be minimized if accurate N exponents are to be obtained.

Experimental Section

Five polystyrene standards with molecular weights from 4.4 × 10^6 to 30 × 10^6 were purchased from Polymer Laboratories, Toyo Soda, and Polysciences. Solutions were prepared by dissolving the samples in spectroscopic-grade toluene clarified by prior filtration through 0.2-μM Millipore filters. All concentrations were well below the overlap concentration c^*, estimated from the reciprocal of the intrinsic viscosity. Sample characterizations were made by static light scattering, using an apparatus constructed in this laboratory and described elsewhere.[17] The apparatus performed satisfactorily to scattering angles as low as 20° using 633-nm light. Solvents and solutions were filtered directly into the scattering cell through 0.5-μm Millipore filters. The weight-average molecular weights, determined from Zimm plot analyses, are tabulated in Table I, along with the radii of gyration in the absence of flow. Across the relevant angular range, 20–50°, the Zimm plots did not display the curvatures that might be expected from either polydispersity or higher order terms in the scattering function. The relationship between the z-average radius of gyration and molecular weight is given as $R_g \sim N^{\nu}$, with $\nu = 0.65$. This exponent confirms the goodness of toluene as a solvent; the increase of ν above its expected level for a good solution probably reflects a minor molecular weight polydispersity,[18] a parameter difficult to quantify for such high molecular weight samples. The absolute values of R_g agree quantitatively with those in the literature for the same polymer/solvent system.[18,19]

An opposed jets flow device, similar to that developed by Keller and co-workers, was used to generate stagnation-type uniaxial elongational flow; the device was described previously.[17] Polymer solution was withdrawn through opposing glass jets by a vacuum pump; the vacuum was regulated to control the flow rate. The nominal elongation rate $\dot{\epsilon}$ can be obtained as an average across the region between the jets:[4]

$$\dot{\epsilon} = Q/\pi r^2 d \tag{3}$$

where Q is the total flow rate through the jets, r is the inner radius of the jets, and d is the gap width. Both Q and d were varied.

Measurements of relative flow birefringence (i.e., retardance) δ were conducted with the jets oriented perpendicularly to the

0024-9297/92/2225-7060$03.00/0

Table I
Specifications of the Polystyrene Samples

$M_w \times 10^{-6}$ [a]	$M_w \times 10^{-6}$ [b]	R_g (nm)	$\dot{\epsilon}_c$ (s^{-1})[c]	$\dot{\epsilon}_c$ (s^{-1})[d]
4.4[e]	5.36 ± 0.3	122 ± 4	7096	7500 ± 1000
6.7[f]	7.4 ± 0.3	166 ± 5	4374	4560 ± 400
8.5[e]	9.4 ± 0.2	192 ± 3	3030	3020 ± 400
20[g]	24 ± 1	345 ± 15	748	800 ± 150
30[g]	30.9 ± 2	460 ± 14	513	570 ± 50

[a] Molecular weight provided by the supplier. [b] Weight-average molecular weight determined by static light scattering. [c] Critical strain rate calculated by eq 8 (reciprocal of τ_{Zimm}). [d] Experimentally determined critical strain rate. [e] Supplier: Polymer Laboratories. [f] Supplier: Toyo Soda. [g] Supplier: Polysciences.

incident beam and positioned at the center of the large light scattering cell. During birefringence experiments, the goniometer was rotated to zero scattering angle and crossed polarizers were inserted at 45° to the vertical in both the incident and detection optics; otherwise, the optical arrangement for birefringence was the same as that for static light scattering. The jets were always carefully positioned to ensure that the beam was transmitted through the center of the thin birefringent cylinder observed at the flow device's stagnation point at large $\dot{\epsilon}$. The approximate diameter of this cylinder was 150 μm when 700-μm-diameter jets were employed, while the focused incident beam waist was 115 μm. The transmitted intensity I is given as[2]

$$I = I_0 \sin^2 2\theta \sin 2(\delta/2) \tag{4}$$

where I_0 is the incident intensity, and θ is the angle between the principal axis of the sample's refractive index tensor and the incident polarization. The retardance can be related to the birefringence Δn by

$$\delta = (2\pi/\lambda)\Delta n l \tag{5}$$

where λ is the wavelength, and l is the path length of the birefringent region. Since the birefringence in this flow geometry varies along the beam path, δ and Δn are more properly related through a convolution;[4] however, the size and intensity distribution of the birefringent region was found to vary little with $\dot{\epsilon}$ so the convolution was not needed here. In this setup, $\theta = 45°$; therefore

$$I = I_0 \sin 2(\delta/2) \tag{6}$$

For dilute and semidilute polymer solutions, Δn usually ranges from 10^{-9} to 10^{-6},[19] so to a good approximation

$$I/I_0 \simeq \delta^2/4 + O(\delta^4) \sim \Delta n^2 \tag{7}$$

Visual observations of the birefringence were made in a separate apparatus, also described in ref 17; these observations confirmed the stability of the birefringent zone under all conditions examined.

Results and Discussion

Figure 1 displays the relative flow birefringence of a 100 ppm solution of the 9.4×10^6 molecular weight polystyrene as a function $\dot{\epsilon}$. The error bars represent the data scatter for three separate flow runs employing a single solution. Here, and in all cases presented, the birefringence rises rapidly in a narrow window of $\dot{\epsilon}$ before a final saturation to constant intensity; a few samples were discarded from this report because their birefringence rise with $\dot{\epsilon}$ was more gradual, presumably reflecting a larger polydispersity than in the samples selected. The critical strain rate $\dot{\epsilon}_c$, presented in Table 1, is the inflection point of a best-fit curve through the data. As initially suggested by Rabin,[16] the $\dot{\epsilon}_c$ values determined in this fashion agree extraordinarily well with the reciprocal of the Zimm relaxation time, calculated from the formula[20]

$$\tau_{Zimm} = 6.22\Phi_0 R_{g0}{}^3 \eta_s / RT \tag{8}$$

where Φ_0 is the Fox–Flory parameter calculated by Zimm

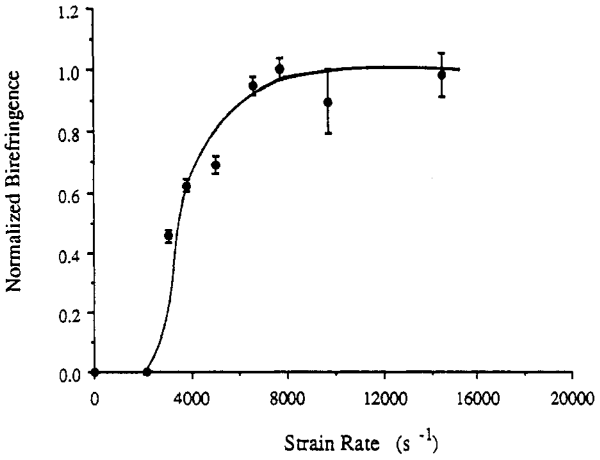

Figure 1. Relative flow birefringence for a 100 ppm solution of the 9.4×10^6 molecular weight polystyrene in toluene as a function of $\dot{\epsilon}$.

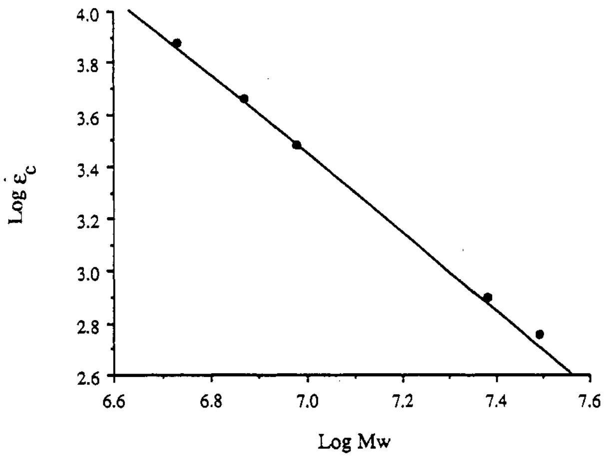

Figure 2. Critical strain rate $\dot{\epsilon}_c$ as a function of molecular weight for polystyrene in toluene. The data points are experimental, whereas the solid line is calculated from eq 8.

$(2.84 \times 10^{23}{}_{22})$, R_{g0} is the unperturbed radius of gyration of polystyrene at room temperature,[23] η_s is the viscosity of toluene (=0.58 cP), R is the gas constant, and T is the temperature. The close coincidence is demonstrated in Figure 2, where τ_{Zimm} is shown as the solid line. A best-fit line through the data, not shown because it so closely superimposed on the theory line, exhibits a slope of −1.47 ± 0.03 (68% confidence interval). There are other ways to analyze this data: if the critical strain rate were to be defined differently (e.g., with $\dot{\epsilon}_c$ defined at some constant fraction of the saturated intensity) or if the experimental Φ_0 value for this system was imposed, the theory line will shift slightly away from the data; the experimental N exponent, however, persists in the range −1.45 to −1.50 irrespective of the method of data analysis.

These experiments decisively confirm the N dependence of $\dot{\epsilon}_c$ reported previously by both Keller et al.[1,3,5] and Cathey and Fuller.[4] A complete theoretical understanding of the relationship, and why it follows the Zimm scaling, is not available. Neither the −1.8 exponent from dynamic scaling nor the −1.6 exponent from the stability limit of the coiled state can be reconciled with the exponent determined here, as both values lie outside the range of experimental uncertainty. Naive scaling actually predicts an even larger exponent ($3\nu = 1.95$); this value can be dismissed from discussion, however, since our measurement of ν is strongly biased by polydispersity but the N scaling of $\dot{\epsilon}_c$ is not. Our earlier light scattering work indicates that the magnitude of chain deformation near, or even slightly above, $\dot{\epsilon}_c$ remains limited. This result argues against Rabin's second explanation, the suppression of excluded volume upon stretching, since this suppression requires larger chain extensions than observed. The current and previous results together suggest that the relaxation time associated with the fluctuations in the undeformed, equilibrium polymer coil may not be the relevant time scale for flow-induced extension.[15]

Acknowledgment. This work was supported by the National Science Foundation (Grant DMR-9019527).

References and Notes

(1) Farrell, C. J.; Keller, A.; Miles, M. J.; Pope, D. P. *Polymer* **1980**, *21*, 1292.
(2) Fuller, G. G.; Leal, L. G. *Rheol. Acta* **1980**, *19*, 580.
(3) Keller, A.; Odell, J. A. *Colloid Polym. Sci.* **1985**, *263*, 181.
(4) Cathey, C. A.; Fuller, G. G. *J. Non-Newtonian Fluid Mech.* **1990**, *34*, 63.
(5) Narh, K. A.; Odell, J. A.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 335.
(6) Hunkeler, D. J.; Nguyen, T. Q.; Kausch, H. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 667.
(7) de Gennes, P.-G. *J. Chem. Phys.* **1974**, *60*, 5030.
(8) Hinch, D. *J. Phys. Fluids* **1977**, *20*, s22.
(9) Bird, R. B.; Curtiss, C. F.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids*, 2nd ed.; John Wiley & Sons: New York, 1987; Vol. 2.
(10) Brestkin, Y. V.; Saddikov, I. S.; Agranova, S. A.; Baranov, V. G.; Frenkel, S. *Polym. Bull.* **1986**, *15*, 147.
(11) Atkins, E. D. T.; Attwool, P. T.; Miles, M. J. Bristol Conference on Macromolecular Flexibility and Behavior in Solution, Bristol, U.K., 1986.
(12) Odell, J. A.; Keller, A.; Rabin, Y. *J. Chem. Phys.* **1988**, *88*, 4022.
(13) Muller, A. J.; Odell, J. A.; Keller, A. *Polym. Commun.* **1989**, *30*, 298.
(14) Rabin, Y.; Ottinger, H. C. *Europhys. Lett.* **1990**, *13*, 423.
(15) Rabin, Y. In *Polymer Flow Interactions*; Rabin, Y., Ed.; American Institute of Physics, La Jolla Institute: La Jolla, CA, 1985; Vol. 137, p 5.
(16) Rabin, Y. *Phys. Rev. Lett.* **1985**, *55*, 201.
(17) Menasveta, M. J.; Hoagland, D. A. *Macromolecules* **1991**, *24*, 3427.
(18) Appelt, B.; Meyerhoff, G. *Macromolecules* **1980**, *13*, 657.
(19) Seery, T. A. P.; Shorter, J. A.; Amis, E. J. *Polymer* **1989**, *30*, 1197.
(20) Farinato, R. S. *Polymer* **1983**, *29*, 160.
(21) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(22) Konishi, T.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1991**, *24*, 5614.
(23) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1989.