3694 *Macromolecules* **1997,** *30,* 3694−3695

Viscoelastic Properties of Highly Entangled Poly(vinyl methyl ether)

R. M. Kannan[†] **and T. P. Lodge***

Department of Chemistry and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455-0431

Received July 12, 1996
Revised Manuscript Received January 22, 1997

Introduction

Poly(vinyl methyl ether) (PVME) has been widely employed in studies of polymer mixtures, both in the melt and in solution, because it exhibits miscibility with polystyrene (PS) over a wide range of conditions.[1,2] For example, we have employed PVME as a matrix polymer to investigate tracer diffusion of linear and branched PS chains and PS latex particles in semidilute and concentrated solutions and gels.[3−6] Others have examined the phase behavior of PS/PVME blends in the melt, where lower critical solution temperature (LCST) behavior is displayed.[7−12] Diffusion behavior and rheological properties in PS/PVME blends have also been investigated.[13,14] PVME is typically prepared by cationic polymerization, but chain transfer processes keep the average molecular weight low ($M_w \leq 10^5$) and the polydispersity high ($M_w/M_n \geq 2$). Living cationic polymerization of PVME has been demonstrated, but only for $M_w \leq 2 \times 10^4$.[15] One consequence of this is that, so far as we are aware, there have been no studies of the viscoelastic properties of highly entangled PVME samples. To this end we report measurements of the frequency (ω) and temperature (T) dependences of the dynamic shear modulus G^* for a PVME melt with $M_w = 1.3 \times 10^6$ and $M_w/M_n \approx 1.3$.[16] This material was synthesized by cationic polymerization and fractionated as previously described;[17] it has been used as a matrix material in several of our solution diffusion studies.[3,4,6] The resulting information about the molecular weight between entanglements M_e and the monomeric friction factor ζ should facilitate quantitative interpretation of the dynamic properties of melt blends. Furthermore, the frequency dependence of the loss modulus in the entanglement zone is compared with the predictions of recent models.[18−20]

Experimental Section

Determination of T_g. The glass transition temperature T_g of the PVME was determined using a Perkin-Elmer DSC-7 thermal analysis system. The melting temperatures of ice and indium were used as references for temperature calibration. The sample was heated at 10 °C/min under a nitrogen atmosphere. A clear thermal transition was observed between −26 and −20 °C, with a midpoint at −22.9 °C.

Rheology. Rheological measurements were performed on a Rheometrics Solids Analyzer (RSA-II) in the shear sandwich geometry (15.95 mm × 12.65 mm × 0.5 mm). The sample was loaded at 150 °C and then cooled to 50 °C to trim the excess material along the edges. Oscillatory shear experiments were conducted at nine temperatures from −10 to +240 °C under a nitrogen atmosphere. The sample was allowed to equilibrate for 30 min at each temperature before the start of frequency sweep measurements. The storage (G') and loss (G'') moduli were measured over 3.5 decades of frequency (0.02−100 rad/s) at small strains (typically 1% at the lowest temperature and 25% at the highest temperature). The data for various temperatures and frequencies were superimposed in the standard manner.[21] Horizontal shift factors (a_T) were determined by eye, using the data for each temperature plotted as the phase angle δ. The vertical shift factors ($\rho_o T_o/\rho T$), where ρ is the density and the subscript o denotes the reference temperature, were determined using $\rho(T)$ reported by Shiomi *et al.*[10]

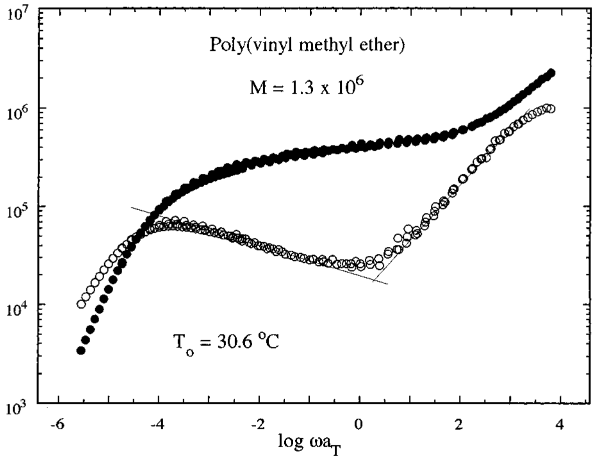

Figure 1. Reduced dynamic shear moduli for high molecular weight poly(vinyl methyl ether). The straight lines are guides to the eye and have slopes of −0.15 and 0.57.

Results and Discussion

The resulting master curves for G'_R and G''_R as functions of reduced frequency ωa_T are shown in Figure 1 (the subscript R, which will be omitted henceforth, indicates that the density correction has been applied). The data extend over approximately 10 decades in reduced frequency, with terminal, plateau, and transition regimes of viscoelastic behavior evident. However, the majority of the data lie in the plateau regime. Overall, the superposition is satisfactory. The value of the plateau modulus G_N^o may be established in several ways.[21,22] The preferred method would be to integrate under the terminal loss peak

$$G_N^o = \frac{2}{\pi}\int_{-\infty}^{\infty} G''(\omega)\,\mathrm{d}\ln\omega \qquad (1)$$

but the data do not extend to sufficiently low frequency to firmly establish the terminal behavior. Consequently, three semiempirical methods were employed: the value of G' at the minimum of G''; the value of G' at the inflection point in G'; the maximum value of G'' in the terminal loss peak, divided by 0.207.[21] All three methods yielded equivalent values, $G_N^o = 0.407 \pm 0.007$ MPa at 30 °C. This corresponds to a molecular weight between entanglements M_e given by[18,22]

$$M_e = \frac{4}{5}\frac{\varrho RT}{G_N^o} = 5100 \qquad (2)$$

The frequency dependence of G'' exhibits two regimes of power law behavior for $\omega\tau_1 > 1$, associated with the entanglement plateau and transition zones of viscoelastic response. In the former, the apparent exponent is approximately −0.15, as shown in Figure 1 (the lines are guides to the eye, not fits). This is close to, but

---

[*] To whom correspondence should be addressed.

[†] Current address: 3M Corporation, 3M Center, St. Paul, MN 55144-1000

S0024-9297(96)01019-4 CCC: $14.00

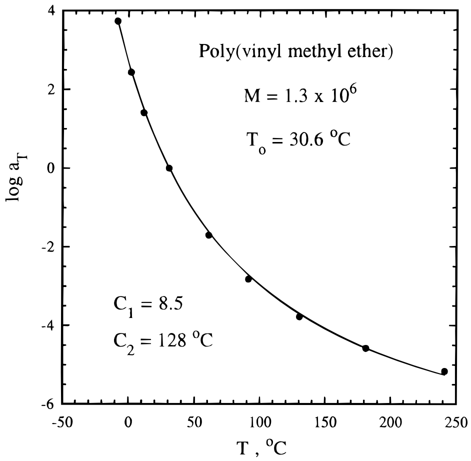

Figure 2. Time–temperature superposition shift factors for poly(vinyl methyl ether), and the fit to the WLF equation for a reference temperature of 30.6 °C.

Table 1. Properties of Poly(vinyl methyl ether)

property	value
M_w, g/mol	1.3×10^6
M_w/M_n	1.3
ρ , g/mL[a]	1.051
T_g, °C	−22.9
G_N^o,[a] MPa	0.407
M_e,[a] g/mol	5100
C_1[a]	8.5
C_2[a] °C	128
C_1^g	14.4
C_2^g, °C	71.5
f_g/B	0.030
$\Delta\alpha$, °C^{-1}	4.2×10^{-4}

[a] At, or relative to, the reference temperature of 30.6 °C.

slightly smaller than, the values recently reported for polybutadiene (−0.18) and polystyrene (−0.23).[23] These entanglement zone exponents are considerably less than the value of −0.5 associated with the Doi–Edwards model,[18] but are at least roughly consistent with the recent mode-coupling theory of entangled polymer dynamics[20] and are a natural consequence of the proposed Baumgaertel–Schausberger–Winter relaxation spectrum.[19] Jackson *et al.*, noted that the value for polybutadiene approaches −0.23 in the high *M* limit, and suggest that the exponent may be universal.[23] The value for PVME does not support this view, although the finite polydispersity may play a role. In the transition zone the exponent is approximately 0.57, which agrees rather well with the Rouse value of 0.5. Corresponding values of 0.71 and 0.67 have been reported for polybutadiene and polystyrene, respectively.[23]

The temperature dependence of the time–temperature superposition shift factor a_T, or equivalently, of the monomeric friction factor ζ is shown in Figure 2. The smooth curve represents the best fit to the Williams–Landel–Ferry (WLF) equation:[21]

$$\log a_T = \frac{C_1(T - T_o)}{C_2 + (T - T_o)} \tag{3}$$

with the reference temperature T_o = 30.6 °C; the resulting values of the WLF coefficients C_1 and C_2 are given in Table 1. This function can then be extrapolated to T_g, and the data can be refitted with T_g as the reference temperature. The resulting WLF parameters C_1^g and C_2^g and the corresponding free volume quantities f_g/B and $\Delta\alpha$ are also given in Table 1. These fits extend up to +241 °C, which is far beyond the canonical domain of validity of the WLF equation, *i.e.*, $T_g \le T \le T_g + 100$ °C. However, the fit is quite good over the entire range. Furthermore, if the fit is restricted to the data with $T \le 91$ °C, the values of C_1^g and C_2^g change by only 2–4%.

Summary

We report values for the plateau modulus G_N^o = 0.407 MPa and the molecular weight between entanglements, M_e = 5100 g/mol for poly(vinyl methyl ether), on the basis of the viscoelastic measurements on a high molecular weight sample. The loss modulus exhibits power law behavior in both the entanglement and transition zones. In the former regime, the associated exponent of approximately −0.15 is not consistent with the predictions of the Doi–Edwards model, but is in reasonable accord with the BSW relaxation spectrum and mode-coupling theory. The temperature dependence of the monomeric friction factor is extracted from the time–temperature superposition shift factors.

Acknowledgment. This work was supported by the National Science Foundation, through Grant DMR-9018807. We particularly appreciate the willingness of L. J. Fetters to perform an SEC analysis of the polymer.

References and Notes

(1) Bank, M.; Leffingwell, J.; Thies, C. *Macromolecules* **1971**, *4*, 43.
(2) Kwei, T. K.; Nishi, T.; Roberts, R. F. *Macromolecules* **1974**, *7*, 667.
(3) Wheeler, L. M.; Lodge, T. P. *Macromolecules* **1989**, *22*, 3399.
(4) Lodge, T. P.; Markland, P.; Wheeler, L. M. *Macromolecules* **1989**, *22*, 3409.
(5) Rotstein, N. A.; Lodge, T. P. *Macromolecules* **1992**, *25*, 1316.
(6) Won, J.; Onyenemezu, C.; Miller, W. G.; Lodge, T. P. *Macromolecules* **1994**, *27*, 7389.
(7) Shibayama, M.; Yang, H.; Stein, R. S.; Han, C. C. *Macromolecules* **1985**, *18*, 2179.
(8) Han, C. C.; Bauer, B. J.; Clark, J. C.; Muroga, Y.; Matsushita, Y.; Okada, M.; Tran-cong, Q.; Chang, T. *Polymer* **1988**, *29*, 2003.
(9) Yang, H.; Hadziioannou, G.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *21*, 159.
(10) Shiomi, T.; Hamada, F.; Nasako, T.; Yoneda, K.; Imai, K.; Nakajima, A. *Macromolecules* **1990**, *23*, 229.
(11) Hammouda, B.; Bauer, B. J. *Macromolecules* **1995**, *28*, 4505.
(12) Janssen, S.; Schwahn, D.; Springer, T.; Mortensen, K. *Macromolecules* **1995**, *28*, 2555.
(13) Green, P. F.; Adolf, D. B.; Gilliom, L. R. *Macromolecules* **1991**, *24*, 3377.
(14) Takahashi, Y.; Suzuki, H.; Nakagawa, Y.; Noda, I. *Macromolecules* **1994**, *27*, 6476.
(15) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265.
(16) Recent chromatographic analysis confirmed the polydispersity of the sample to be 1.3 and gave a peak molecular weight of *ca.* 1.1×10^6 g/mol, based on polystyrene standards and universal calibration.
(17) Bauer, B. J.; Hanley, B.; Muroga, Y. *Polymer Commun.* **1989**, *30*, 20.
(18) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(19) Baumgaertel, M.; Schausberger, A.; Winter, H. H. *Rheol. Acta* **1990**, *29*, 400.
(20) Schweizer, K. S.; Szamel, G. *Transp. Theory Stat. Phys.* **1995**, *24*, 947.
(21) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(22) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.
(23) Jackson, J. K.; De Rosa, M. E.; Winter, H. H. *Macromolecules* **1994**, *27*, 2426.

MA961019I