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Viscosity Characterization of Poly(tetrafluoroethylene) by Centrifuge Ball Viscometry

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ABSTRACT: Low shear rate viscosity measurements of poly(tetrafluoroethylene) (PTFE, also known as Teflon, a registered trademark of Du Pont) melts have been performed at different temperatures by using the centrifuge ball viscometer (CBV). An average measured viscosity value of 5.2×10^9 Pa·s was obtained for PTFE-T60 at 380 °C. The viscosity η (Pa·s) was computed by using an empirical relation $a_c(g) = (4.29 \pm 0.08) \times 10^2(\eta V_\infty)^{0.856\pm0.004}$ (or $=79(\eta V_\infty)^{0.86}$) with a_c ($a_c > 1.1 \times 10^{-2}$ gravity) and V_∞ being respectively the acceleration and the terminal velocity of a stainless steel ball of 1.58 (or 4.76) ± 0.01 mm diameter moving in the fluid (e.g., polymer melts) contained in a horizontal cylindrical glass tube having an inside diameter of 4.26 (or 9.99) ± 0.01 mm. Temperature-dependent viscosities of PTFE melts were obtained, and the activation energy E_a covered a narrow range of 17−18 kcal/mol. The zero shear viscosity, η^0 (Pa·s), and the molecular weight, M_w, of three PTFE melts obey the relationship $\eta^0 = (4.94 \pm 0.07) \times 10^{-14} M_w^{\alpha=3.2\pm0.1}$ at 380 °C. Based on this relationship, the molecular weight (MW) of PTFE-T60 is estimated to be 1.6×10^7. If $\alpha = 3.4$, MW $= 1.4 \times 10^7$ for PTFE-T60.

Introduction

Poly(tetrafluoroethylene) (PTFE, also known as Teflon, a Du Pont trademark) has been used widely as cookware coatings, or isolators to heat and chemical attack under extreme conditions, because of its inertness to most chemicals including strong acids and bases. Its high-temperature stability remains unmatched among all known common polymers. The properties of PTFE have been reported extensively in the literature.[1−18] The *absolute* molecular weight of two PTFE samples has been determined successfully by laser light scattering.[6−8] There are several relative methods to determine the molecular weight (MW) of polymers. Among them are the stress relaxation,[14] the zero strength time (ZST),[17,19] the crystallinity,[20,21] the specific gravity,[21] and the melt viscosity measurements.[18] In addition, end-group analysis has been used to compute the number-average molecular weight.[20] Here, we report a detailed study of poly(tetrafluoroethylene) melt viscosity as a function of molecular weight and temperature by using a centrifuge ball viscometer (CBV). A brief description of the CBV is presented in the Experimental Section, with the details having been described elsewhere.[22]

Experimental Section

1. Polymer Characteristics and Sample Preparation. Four PTFE polymers (courtesy of Du Pont Experimental Station, Wilmington, DE; see Table 1) were used in the present study. The PTFE polymer powder was pressed into a cylindrical rod at room temperature. The compressed PTFE rod of known weight was inserted into a cylindrical glass cell of 4.26 ± 0.01 mm i.d. except for PTFE-T60 where the inside diameter of the cylindrical glass cell was changed to 9.99 ± 0.01 mm. Then a 1.58 ± 0.01 mm diameter stainless steel ball (or 4.76 ± 0.01 mm diameter for the larger cylindrical glass cell) was introduced to the side of the cylindrical wall and vacuum sealed. The melt density could be estimated from the volume of the melt and the weight of the melt in the cylindrical glass tube at different temperatures.[23]

Table 1. Molecular Parameters of PTFE Polymers

sample	$M_w \times 10^{-6}$ [a]	M_w/M_n [a]	$M_w \times 10^{-6}$ [b]	M_w/M_n [b]	η^0 (Pa·s)	T (°C)
PTFE-5	2.3	8.2	2.1	2.0	$(8.9 \pm 0.3) \times 10^6$	406
PTFE-6	0.34	2.8	0.26	2.1	$(2.3 \pm 0.1) \times 10^4$	379
PTFE-7	1.8	4.3			$(3.8 \pm 0.2) \times 10^6$	387
PTFE-T60	16[c]				$(5.2 \pm 0.7) \times 10^9$	380

[a] Rheological data.[9] [b] Laser light scattering data.[6−8] [c] MW of PTFE-T60 determined in this study.

2. Centrifuge Ball Viscometer (CBV). The essential features of the centrifuge ball viscometer have been presented in detail elsewhere.[22] A brief description is provided here for completeness. The centrifuge ball viscometer was equipped with a personal computer (PC)-based motion controller as shown schematically in Figure 1. The speed of the rotor could be kept either constant or decreased so as to yield a constant acceleration for the moving ball. The PC-based motion controller (EPC7252, Encoder Products Co.) could vary the rotor speed ranging from 1 to 5000 revolutions/min (rpm) to within a ±0.01 rpm precision. The pulsed light was triggered synchronously by a timer/counter board (CTM-05, MetraByte Co.).

The centrifuge ball viscometer was equipped with a microscope for visual observation of the ball or a CCD (charge-coupled device) camera, as shown schematically in Figure 1. In order to keep a constant acceleration for a moving sphere in the centrifuge cell, the following relation must hold

$$\mathrm{rpm}_2 = \mathrm{rpm}_1(P_1/(P_1 + (t_2 - t_1)V))^{1/2} \qquad (1)$$

where V is the ball velocity; rpm_1 and rpm_2 are respectively the revolutions per minute of the motor for the ball at position P_1 (measured from the rotation axis) and time t_1 and at position P_2 and time t_2. The acceleration a_c of a ball at position P (cm) with the rotor speed (rpm) can be described by $a_c = P\omega^2 = 1.118 \times 10^{-5}P(\mathrm{rpm})^2$ (unit of gravity g) where ω is the angular velocity of the motor. By using an appropriate centrifugal acceleration, the measurement time to determine the ball velocity could be cut down dramatically for highly viscous polymer melts. The CBV could be used to measure the low shear rate viscosity of highly viscous fluids by applying different accelerations. The CBV is capable of measuring the fluid viscosity ranging from $\sim10^0$ to $\sim10^{12}$ Pa·s by applying accelerations ranging from 10^{-3} to $7 \times 10^2 g$ and by using different ball and sample cell diameters. The temperature

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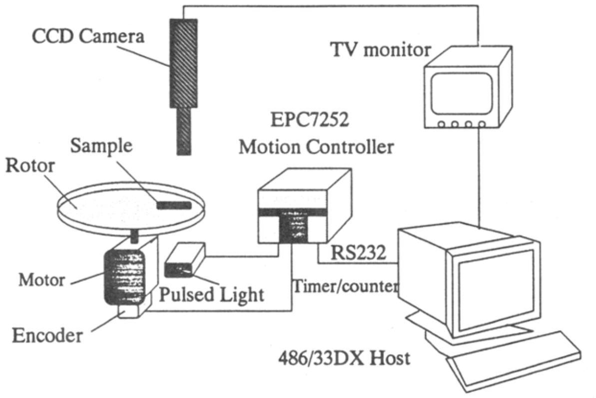

Figure 1. Schematic diagram of centrifuge ball viscometer.

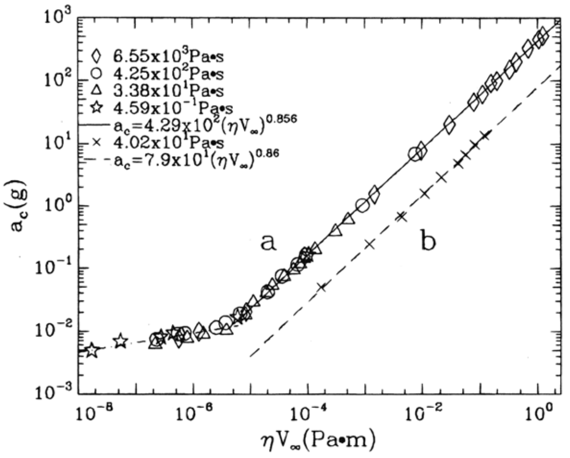

Figure 2. log–log plot of a_c vs ηV_∞. Curve a:[22] ball/tube diameter = 1.58/4.26. Curve b: ball/tube diameter = 4.76/9.99.

inside the sample chamber can be controlled from ambient to around 500 °C. The viscosity (η) was determined by measuring the terminal velocity of the sphere at a constant centrifugal acceleration. By testing several different viscosity standards with a density of 0.88 g/cm^3 and by using a 1.58 ± 0.01 mm diameter steel ball and a 4.26 ± 0.01 mm i.d. cylindrical glass cell. We obtained the following empirical relationship

$$a_c = b(\eta V_\infty)^c \tag{2}$$

with $b = (4.29 \pm 0.08) \times 10^2$ [g/(Pa·m)^c] and $c = 0.856 \pm 0.004$ for $a_c > 1.1 \times 10^{-2} g$; $b = (2.16 \pm 0.04) \times 10^{-1}$ [g/(Pa·m)^c] and $c = 0.15 \pm 0.02$ for $a_c < 1.1 \times 10^{-2} g$.

For the 4.76 mm ball in a 9.99 mm i.d. tube, only one viscosity standard was used. The empirical relationship in eq 2 has the numerical values $b = 79$ and $c = 0.86$ for $a_c > 1.1 \times 10^{-2} g$. The shear rate ($\dot{\gamma}$) at the terminal velocity V_∞ can be estimated by the relation[24]

$$\dot{\gamma} = 4dV_\infty/(D^2 - d^2) \tag{3}$$

where D and d are respectively the tube inside diameter and the ball diameter.

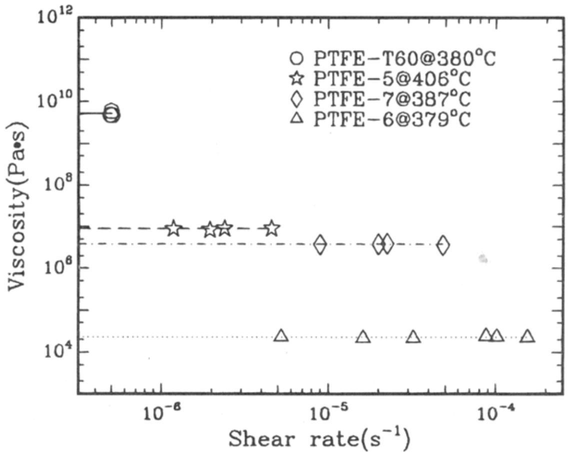

Figure 3. Viscosity versus shear rate of three melts at different temperatures. η^0 (Pa·s) values for PTFE-5, PTFE-6, and PTFE-7 at different temperatures are $(8.9 \pm 0.3) \times 10^6$, $(2.3 \pm 0.1) \times 10^4$, and $(3.8 \pm 0.2) \times 10^6$, respectively. For PTFE-T60, the melt viscosity measured at a low shear rate of about 5×10^{-7} s^{-1} is $(5.2 \pm 0.7) \times 10^9$ Pa·s. The viscosities of PTFE melts at fixed temperatures over the range of shear rates as shown in Figure 3 are presented in order to show the reproducibility of the CBV measurements for PTFE melts. PTFE-5 at 406 °C: 8.91, 8.40, 9.05, 9.01 × 10^6 Pa·s. PTFE-6 at 379 °C: 2.31, 2.21, 2.22, 2.45, 2.34, 2.28 × 10^4 Pa·s. PTFE-7 at 387 °C: 3.80, 3.85, 3.98, 3.63 × 10^6 Pa·s. PTFE-T60 at 380 °C: 4.89, 4.77, 6.00 × 10^9 Pa·s.

Results and Discussion

The calibration results for the two ball/tube pairs are shown in Figure 2. Figure 3 shows the shear rate dependence of viscosities for different PTFE samples at various temperatures (see also Table 1). The centrifuge ball viscometer has the advantage of approaching the lower limit in the shear rate by applying only a very small acceleration and by measuring the moving ball over a relatively long period of time. These low shear rate viscosity (η^0) measurements seem to fall within the Newtonian fluid region where the viscosity is independent of the shear rate. Figure 4 shows a long time measurement of a moving ball in the PTFE-T60 melts. Figure 4a shows the moving distance of the ball versus time plot for a 4.76 mm diameter stainless steel ball in a 9.99-mm-i.d. tube with PTFE-T60 melt. The terminal velocity of the stainless steel ball was determined to be 1.60×10^{-7} cm/s within a period of 2.2×10^4 s at 380 °C. The shear rate at this terminal velocity was 4.98×10^{-7} s^{-1} based on eq 3. The PTFE melt viscosity was determined to be 6.0×10^9 Pa·s according to the eq 2 with $b = 79$ and $c = 0.86$. The velocity of the stainless steel ball moved faster after 2.2×10^4 s. After $\sim 2 \times 10^4$ s, we observed a light brownish color with the sample. The possibility of degradation could not be excluded. Thus, the higher velocity value after 2.2×10^4 s was not taken seriously. Figure 4b shows another run of PTFE-T60 at the same temperature but with a slight variation in sample preparation. We also stopped the rotation of the rotor at $t = 1.044 \times 10^4$ s and restarted the experiment at time 1.069×10^4 s. The terminal velocities for the former and latter time periods were 2.00×10^{-7} and 2.03×10^{-7} cm/s, respectively. Their viscosities and shear rates were 4.9×10^9 Pa·s, 4.91×10^{-7} s^{-1} and 4.8×10^9 Pa·s, 5.03×10^{-7} s^{-1}, respectively. The average viscosity of these three measured values was $(5.2 \pm 0.7) \times 10^9$ Pa·s. It should be noted that for the PTFE-T60 melt we made the viscosity measurements mainly at only one low shear rate of about 5×10^{-7} s^{-1}. Thus, we could not claim, in a strict sense, that the η value of $(5.2 \pm 0.7) \times 10^9$ Pa·s was the zero shear rate viscosity. However, as the measurement time was long (Figure 4.1) and the main aim of the present paper was to demonstrate that we could indeed measure, for the first time to our knowledge, the melt viscosity of a commercial Teflon sample, the shear rate dependence of PTFE-T60 melt was not investigated. Parts a and b of Figure 4 show no evidence of a delayed elastic contribution even for short

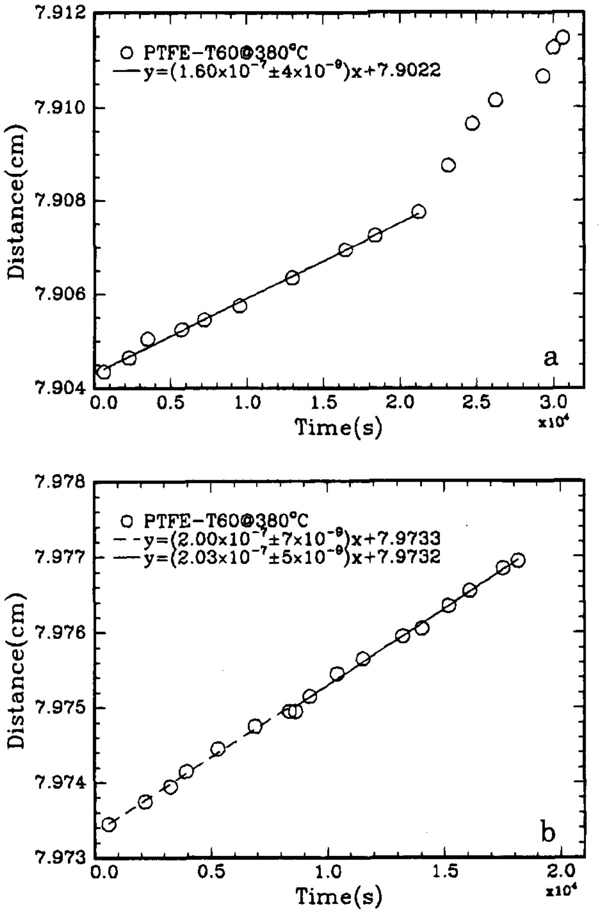

Figure 4. Distance versus time plot for PTFE-T60 polymer at 380 °C. Ball diameter = 4.76 ± 0.01 mm; tube inside diameter = 9.99 ± 0.01 mm. (a) The sample was evacuated under vacuum at room temperature for 10 days before sealing. (b) The sample was evacuated under vacuum at room temperature for ~8 h flushed several times with ultradry nitrogen before sealing.

times, as indicated by the constant slopes within $\sim 10^3$ s after the start of the measurement. The reason for the shorter than expected relaxation time is not clear, although it is noted that the ball velocity was $\sim 2 \times 10^{-7}$ cm/s and the viscosity value was somewhat lower than expected.

Figure 5 shows an Arrhenius plot of four different molecular weights (MWs) of PTFE. The least-squares fitted equations together with some experimental results are listed in Table 2. The activation energy of PTFE revealed a barely detectable temperature dependence, if any, as shown in Figure 6. The average activation energy E_a was about 17.4 kcal/mol, which reduced the great spread of values (8–36 kcal/mol[12,16,18]) to be found in the literature. The activation energy seemed to remain constant at these molecular weights, with the values agreeing to within experimental error limits.

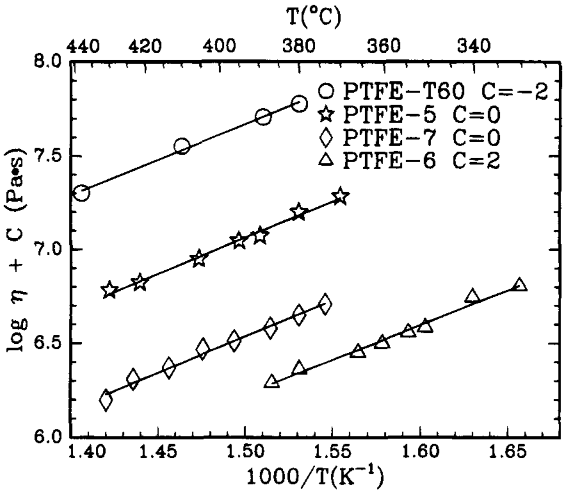

Figure 5. Arrhenius plot of melt viscosities of different MW PTFE polymer melts. Least-squares fitting of experimental data yields the empirical equations on the temperature dependence of the PTFE polymer melt viscosities as listed in Table 2.

Table 2. Temperature Dependence of Low Shear Rate Viscosity of PTFE Melts

			η (Pa·s)	
	T (°C)	log(η)	exptl	calcd
	$\log(\eta) = 3.81 \times 10^3/(T + 273.15) + 3.96$			
PTFE-T60	380	9.79	6.14×10^9	6.01×10^9
	389	9.71	5.12×10^9	5.11×10^9
	410	9.53	3.41×10^9	3.58×10^9
	438	9.31	2.05×10^9	2.00×10^9
	$\log(\eta) = 3.58 \times 10^3/(\mathrm{T} + 273.15) + 1.29$			
PTFE-5	380	7.18	1.52×10^7	1.58×10^7
	395	7.05	1.12×10^7	1.11×10^7
	422	6.82	6.55×10^6	6.66×10^6
	430	6.76	5.70×10^6	6.05×10^6
	$\log(\eta) = 3.84 \times 10^3/(T + 273.15) + 0.774$			
PTFE-7	380	6.65	4.15×10^6	4.47×10^6
	404	6.44	2.77×10^6	2.95×10^6
	423	6.29	1.95×10^6	2.04×10^6
	431	6.23	1.70×10^6	1.58×10^6
	$\log(\eta) = 3.69 \times 10^3/(T + 273.15) - 1.32$			
PTFE-6	330	4.81	6.40×10^4	6.40×10^4
	340	4.71	5.10×10^4	5.56×10^4
	360	4.52	3.28×10^4	3.17×10^4
	380	4.34	2.20×10^4	2.31×10^4
	400	4.17	1.49×10^4	
	420	4.01	1.03×10^4	
	440	3.87	7.34×10^3	

Figure 7 shows a plot of viscosity of PTFE versus molecular weight at 380 °C. At 380 °C, the values of K and α in the viscosity vs molecular weight equation with η^0 (Pa·s) = $K(M_w)^\alpha$ have $K = (4.94 \pm 0.07) \times 10^{-14}$ and $\alpha = 3.2 \pm 0.1$, which is reasonably close to the 3.4 exponent. The results on lower MW PTFE samples are in good agreement with earlier studies of Tuminello *et al.*[9] who used a different viscosity method. Thus, if we were to extend the empirical power law to the viscosity of PTFE-T60, a η^0 value of 5.2×10^9 Pa·s at 380 °C would correspond to a molecular weight of PTFE-T60 of 1.6×10^7. If we were to take the exponent α to be 3.4, then $K' = 2.81 \times 10^{-15}$ and the MW of PTFE-T60 would have a value of 1.4×10^7. By using the semiempirical melt viscosity relations of Fox and Allen[25] and Berry and Fox,[26] Bates and Stockmayer[27] estimated a viscosity equation $\log \eta = 10 \pm 1 + 3.4 \log(10^{-6}\mathrm{MW})$ for the four-state model, with η expressed in P ($\equiv 0.1$ Pa·s). The estimated value of K' ($= 10^{-11.4}$ for the viscosity equation (20) in ref 27) appears to be too large when compared with our experimentally determined K' value. This value of the molecular weight ($\sim 1.5 \times 10^7$) is also consistent with earlier estimates of molecular weights of commercial PTFEs exhibiting a bimodal MW distribution centered around 5×10^6 and 5×10^7.[28] The difference in MW (e.g., 1.4×10^7 vs 1.6×10^7 mol) over the MW range of 10^5–10^7 (see Table 1) is the order of uncertainty of the present experiment. Thus, in the following analysis, we shall use $\alpha = 3.4$. The centrifuge

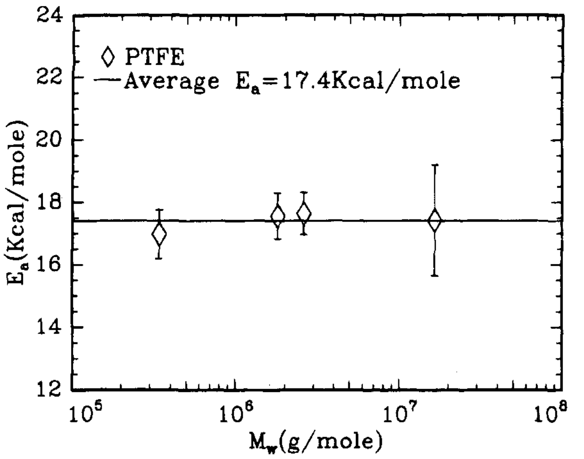

Figure 6. Activation energy of PTFE polymers which remained relatively constant with increasing molecular weight.

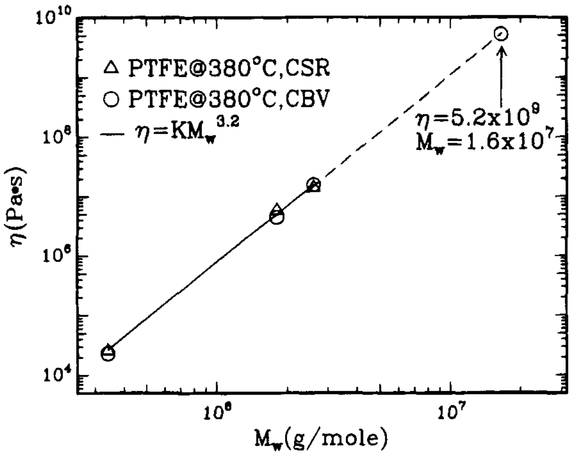

Figure 7. Viscosity of PTFE polymer melts versus molecular weight at 380 °C. CSR denotes constant stress rheometer with data from ref 9. For PTFE-T60, we only measured a low shear rate viscosity and used its value to compute the molecular weight according to the equation η^0 (Pa·s) = KM_w^α. The experimental results are listed as follows. $M_w = 3.40 \times 10^5$, 1.80×10^6, 2.60×10^6, and (1.6×10^7). Viscosity = 2.31×10^4, 4.47×10^6, 1.58×10^7, and 5.22×10^9. A least-square fitting of the viscosity scaling relation yields $\log(\eta) = 3.18 \log(M_w) - 13.21$. With α fixed at 3.40, $\log(\eta) = 3.40 \log(M_w) - 14.6$.

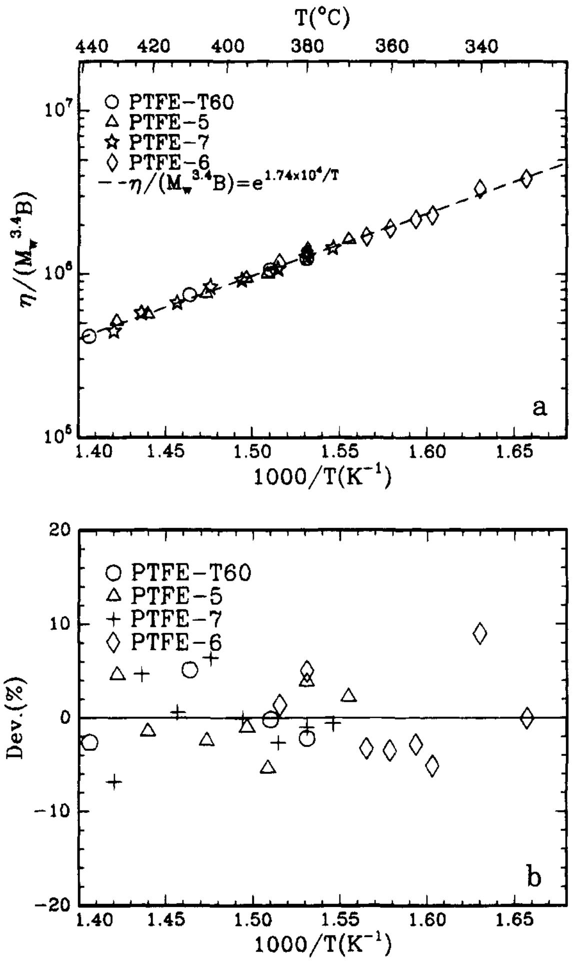

Figure 8. (a) Plot of $\eta/(M_w^{3.4}B)$ vs $1/T$. All four PTFE polymer data can be overlapped well on a master curve with different activation energies E_a. (b) Deviation of $\eta/(M_w^{3.4}B)$ vs $1/T$.

ball viscometer should be a good tool to extract the molecular weight of high-MW polymers.

Generally speaking, the viscosity is a function of various parameters, such as temperature, pressure, molecular weight, and shear rate. The relationship among these variables can be expressed by the following general formula:[29-31]

$$\eta = B(M_w)^\alpha e^{E_a/RT} f(p,\dot{\gamma}) \qquad (4)$$

where B is a proportionality constant and $f(p,\dot{\gamma})$ is a function of pressure and rate of shear, respectively. As we have measured the temperature and the molecular weight dependence of the PTFE melt, the combined data at constant pressure and very low shear rates can be represented by the equation

$$\eta = B(M_w)^{3.4} e^{E_a/RT} \qquad (5)$$

where we have used α = 3.4. It should be noted that with $B \propto M_w^{-\alpha}$ the constant B does not have the same meaning in eqs 4 and 5. From eqs 2 and 5, we have the relation $A = B(M_w)^{\alpha=3.4}$. Equation 5 can be rewritten as

$$\eta/(M_w)^{3.4} = Be^{E_a/RT} \qquad (6)$$

with $B = \eta/(M_w^{3.4}e^{E_a/RT})$. Then all the viscosity data can be plotted in one master curve. Figure 8a shows that all the data for the three PTFE polymers can be merged into one master curve with an average activation energy E_a of 17.4 kcal/mol. Figure 8b shows that the deviation of the measured values of $\eta/(M_w^{3.4}B)$ from eq 6 based on the assumption of constant activation energy is within the experimental error limits.

We have come to a full circle by comparing our results with the pioneering work of Bates and Stockmayer,[27] published in the first (**1968**) issue of *Macromolecules*. Bates and Stockmayer estimated an apparent activation energy of about 25 kcal/mol, which was somewhat smaller than the figure of about 35 ± 5 kcal/mol, derived from the creep data of Nishioka and Watanabe.[18] On the other hand, our value of 17 kcal/mol has confirmed the remarkable estimates made by Bates and Stockmayer close to 30 years ago!

Conclusion

The centrifuge ball viscometer (CBV) has been a very useful instrument for investigating the low shear rate viscosity of high molecular weight polymer melts. We tested the viscosity behavior of three different molecular weight PTFE polymers at various temperatures. The

PTFE melt viscosity agreed reasonably well with the 3.4 exponent for the viscosity−molecular weight relationship. A master curve can be formulated by taking into account the molecular weight and temperature dependence of viscosity for PTFE. Thus, the CBV could become a powerful tool to determine the molecular weight of poly(tetrafluoroethylene) because of its ability to have a closed environment for the sample chamber, to operate at high temperatures and to measure the low shear rate viscosity within a reasonable time period.

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References and Notes

(1) Fontanella, J. J.; Wintersgill, M. C. *Macromolecules* **1994**, *27*, 610.
(2) Pieper, T.; Kilian, H.-G. *Adv. Polym. Sci.* **1993**, *108*, 49.
(3) Starkweather, H. W., Jr.; Avakian, P.; Matheson, R. R., Jr.; Fontanella, J. J.; Wintersgill, M. C. *Macromolecules* **1992**, *25*, 1475.
(4) Allmer, K.; Feiring, A. E. *Macromolecules* **1991**, *24*, 5487.
(5) Starkweather, H. W., Jr.; Avakian, P.; Matheson, R. R., Jr.; Fontanella, J. J.; Wintersgill, M. C. *Macromolecules* **1991**, *24*, 3853.
(6) Chu, B.; Wu, C.; Buck, W. *Macromolecules* **1989**, *22*, 831.
(7) Chu, B.; Wu, C.; Buck, W. *Macromolecules* **1988**, *21*, 397.
(8) Chu, B.; Wu, C.; Zuo, J. *Macromolecules* **1987**, *20*, 700.
(9) Tuminello, W. H.; Treat, T. A.; English, A. D. *Macromolecules* **1988**, *21*, 2606.
(10) Wu, S. *Polym. Eng. Sci.* **1988**, *28*, 538.
(11) Natarajan, R. T.; Davidson, T. *J. Polym. Sci.* **1972**, *A10*, 2209.
(12) Ajroldi, G.; Garbuglio, C.; Ragazzini, M. *J. Appl. Polym. Sci.* **1970**, *14*, 79.
(13) Tobolsky, A. V.; Takahashi, M. *J. Appl. Polym. Sci.* **1963**, *7*, 1341.
(14) Tobolsky, A. V.; Katz, D.; Eisenberg, A. *J. Appl. Polym. Sci.* **1963**, *7*, 469.
(15) Tobolsky, A. V.; Katz, D.; Eisenberg, A. *J. Polym. Sci.* **1963**, *A1*, 483.
(16) Case, L. C. *J. Appl. Polym. Sci.* **1960**, *3*, 254.
(17) Nishioka, A.; Matsumae, K.; Watanabe, M.; Tajima, M.; Owaki, M. *J. Appl. Sci.* **1959**, *2*, 114.
(18) Nishioka, A.; Watanabe, M. *J. Polym. Sci.* **1957**, *24*, 298.
(19) Nishioka, A. *J. Polym. Sci.* **1957**, *26*, 107.
(20) Sperati, C. A.; Starkweather, H. W. *Adv. Polym. Sci.* **1961**, *2*, 465.
(21) Moynihan, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 1045.
(22) Linliu, K.; Yeh, F.; Shook, J. W.; Tuminello, W. H.; Chu, B. *Rev. Sci. Instrum.* **1994**, *65*, 3823.
(23) Zoller, P. *J. Appl. Polym. Sci.* **1978**, *22*, 633.
(24) Briscoe, B.; Luckham, P.; Ren, S. *Colloids Surf.* **1992**, *62*, 153.
(25) Fox, T. G.; Allen, V. r. *J. Chem. Phys.* **1964**, *41*, 344.
(26) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 26.
(27) Bates, T. W.; Stockmayer, W. H. *Macromolecules* **1968**, *1*, 17.
(28) Starkweather, H. W.; Wu, S. *Polymer* **1989**, *30*, 1669.
(29) Fox, T. G.; Flory, P. J. *J. Am. Chem. Soc.* **1948**, *70*, 2384.
(30) Bartenev, G. M. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 3417.
(31) Kumar, N. G. *J. Polym. Sci., Macromol. Rev.* **1980**, *15*, 255.

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