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Viscosity of ethylene/tetrafluoroethylene alternating copolymers

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Low shear rate viscosity measurements of alternating copolymers of ethylene and tetrafluoroethylene (PETFE) melts have been performed at different temperatures by using the centrifuge ball viscometer. The viscosity η (Pa s) could be obtained with an empirical relation, $a_c=(4.29\pm0.08)\times10^2(\eta V_\infty)^{0.856\pm0.004}$, with a_c and V_∞ being, respectively, the acceleration ($g=9.8\,\mathrm{m\,s^{-2}}$) and the terminal velocity ($\mathrm{m\,s^{-1}}$) of a stainless steel ball of 1.58 mm diameter moving in the polymer melt, which was flame sealed in a horizontal cylindrical glass tube of 4.26 mm diameter. For the temperature dependence of the viscosity, an activation energy E_a of 15.3 kcal mol^{-1} was determined. The activation energy for PETFE is between 5.7–14.6 kcal mol^{-1} for polyethylene (PE) and 18–36 kcal mol^{-1} for tetrafluoroethylene (PTFE). A relationship between the zero shear rate viscosity η_0 (Pa s) and the molecular weight M_w (g mol^{-1}) of PETFE copolymer melts at 280°C [$\eta_0=(1.23\pm0.02)\times10^{-16}(M_w)^{3.43\pm0.06}$] should permit us to determine the molecular weight of PETFE with the centrifuge ball viscometer.

(Keywords: low shear rate viscosity; molecular weight; activation energy)

INTRODUCTION

Polymer melts often exhibit non-Newtonian fluid behaviour even at fairly low shear rates, i.e. the viscosity decreases with increasing shear rate. At very low shear rates ($\dot{\gamma}\rightarrow0$), the polymer melt behaves like a Newtonian fluid in which the viscosity is independent of shear rate. The characteristics of alternating copolymers of ethylene and tetrafluoroethylene (PETFE; also known as TEFZEL, a registered trademark of Du Pont) has been studied successfully by laser light scattering (LLS)[1–4], rotational oscillatory and constant stress rheometry (ROCSR)[5,6] and high-temperature capillary viscosimetry (HTCV)[7].

By using the centrifuge ball viscometer[8,9], the relationship between the molecular weight (M_w) and the zero shear rate viscosity (η_0) can be described by the well known (usually, 3.4 power law for linear polymers) empirical formula:

$$\eta_0(\mathrm{Pa\,s})=K[M_w(\mathrm{g\,mol^{-1}})]^\alpha \qquad (1)$$

where K is a proportionality constant and α is the power law exponent. In this paper, the detailed viscosity studies of three different molecular weights of PETFE melts over a temperature range of 272.3–349.5°C, as well as the experimental determination of constants K and α for the PETFE copolymer melts at 280°C, are presented.

EXPERIMENTAL

Copolymer characteristics

Three PETFE copolymers (provided by W. Buck at Du Pont), with sample notation TEFZEL 280, 200 and 210, and their characteristics as studied[1–7] by LLS, ROCSR and HTCV are listed in *Table 1*.

Sample preparation

The PETFE copolymer pellets were weighed and inserted into the precision glass tubing (4.26 ± 0.001 mm i.d.) which had been sealed at one end and put in the preheated thermostat block at about 280°C. Solid pellets became soft and molten so that they could be pressed into one solid piece without any air bubble inside the solid melt. Then a stainless steel ball (1.58 mm ± 0.001 mm diameter) was inserted into the tube touching the side wall of the horizontal cylindrical tube facing the ground and vacuum sealed. Densities of the melt at different temperatures could be estimated from the volume of the melt in the tube and its weight.

Centrifuge ball viscometer

A new high temperature centrifuge ball viscometer (CBV) has been developed to measure the highly viscous polymer melts as a function of shear rate. The details of the instrument have been given elsewhere[8,9]; the essential features of the CBV are described briefly here. The rotor has a radius of 95 mm and can accommodate six samples for each run. The sample chamber can be as long as 90 mm with a maximum tube diameter of 12 mm. The d.c. motor (92A4-22T, Encoder Products Co.) can

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Table 1 Molecular parameters of TEFZEL copolymers

Samples	$M_w\times10^{-5}$* ($g\,mol^{-1}$)	M_w/M_n*	$M_w\times10^{-5}$† ($g\,mol^{-1}$)	M_w/M_n†	η^0(280°C)‡ (Pa s)
TEFZEL 280	11.6	1.4	12.0	2.7	$(9.2\pm0.4)\times10^4$
TEFZEL 200	9.0	1.3	9.1	2.6	$(3.5\pm0.3)\times10^4$
TEFZEL 210	5.4	1.3	5.3	2.9	$(6.2\pm0.3)\times10^3$

* Laser light scattering data[1–4]
† Rheological data[5,6]
‡ Values were computed from η values determined at different shear rates, see *Figure 2*

vary the rotation speed from 1 to 5000 rev min^{-1} (±0.01 rev min^{-1}). The pulsed light is triggered synchronously by a timer/counter board (CTM-05, MetraByte Co.) which acquires the signal from the encoder built in the motor and then sends the signal to trigger the strobe light. The timer/counter board is computer-programmed to adjust the phase of the rotor by 1, 10 or 120° or in finer steps of either 0.64 or 0.18° per step in order to locate the specific sample in alignment with the viewing microscope. A translational stage ($\pm1\,\mu$m precision) in combination with the viewing microscope is used to measure the ball displacement in the horizontal centrifuge tube.

The rotation speed of the rotor was controlled by a motion controller (EPC7252, Encoder Products Co.) which was connected to a 486/DX33 personal computer as shown schematically in *Figure 1*. This centrifuge has two operation modes for different experimental purposes. One is for studying the phase separation of polymer solutions or blends, and the other is for measuring the viscosity of polymer solutions or melts. For the former purpose, constant high rotation speed provides a centrifugal acceleration for faster observation of boundary formation of viscous polymer solutions or blends in phase separation experiments. For the latter aim, a constant acceleration is desired in order for the ball to reach a constant terminal velocity. In this article, the emphasis is on the viscosity measurements of polymer melts at high temperature.

In order to maintain a constant acceleration for a moving ball in the chamber, the following relation must hold:

$$RPM_2 = RPM_1\{P_1/[P_1+(t_2-t_1)V]\}^{1/2} \qquad (2)$$

where V is the ball velocity; RPM_1 and RPM_2 are, respectively, the rotation speed of the rotor for the ball at position P_1 (measured from the centre of rotation) and time $t=t_1$, and at position P_2 and time $t=t_2$. The centrifugal acceleration a_c of a ball at position P (distance in cm from the rotation axis) and rotor speed RPM is:

$$a_c\,(\text{in unit of gravity } g) = P\omega^2 = 1.118\times10^{-5}P(RPM)^2 \qquad (3)$$

where ω is the angular velocity of the rotor. With the variable centrifugal acceleration, the measurement time to determine the ball velocity could be reduced dramatically for highly viscous polymer melts. The CBV was also capable of measuring the shear-dependent viscosity of non-Newtonian fluids by using different applied accelerations a_c which could be used to control the shear rate. Only a very small amount (0.5 ml) of the fluid was needed for the present set-up. The rotation speed of the motor could be programmed by computer for constant acceleration or constant revolutions per minute.

Table 2 Accessible viscosity range of different viscometers

Viscometer type	Range of accessible η (Pa s)	Reference
Capillary	10^2–10^9	19
Falling ball/needle	10^{-3}–10^4	20
Diamond-anvil cell falling/rolling ball	10^{-3}–10^4	21–23
Diamond-anvil cell centrifuge	10^4–5×10^6	24
Swinging vane	10^{-3}–10^3	25
Stress strain	10^6–10^9	20
Centrifuge ball (CBV)	10^0–10^{12}	8, 9

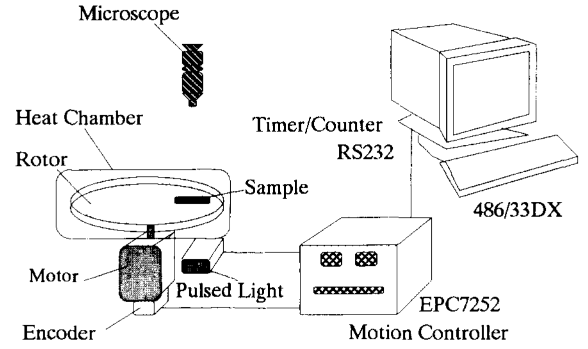

Figure 1 Schematic diagram of centrifuge ball viscometer

The CBV, in principle, is capable of measuring fluid viscosity values ranging from 10^0 to $\sim10^{12}$ Pa s by using a range of different centrifugal accelerations from 10^{-3} to 7×10^2g with various size and density of probe spheres at temperatures from ambient to 480°C. *Table 2* shows the accessible viscosity range of different viscometers[10]. The CBV is superior to other viscometers by its wider attainable viscosity range, a sealable sample chamber and accessible high temperatures up to ~500°C for the present set-up. We tested the CBV by using seven different viscosity standards at different constant centrifugal accelerations. All the experimental data of different viscosity standards can be fitted to a master curve:

$$a_c = b(\eta V_x)^c \qquad (4)$$

with $b=(4.29\pm0.08)\times10^2[g/(\text{Pa m})^c]$ and $c=0.856\pm0.004$ for $a_c>1.1\times10^{-2}g$; $b=(2.16\pm0.04)\times10^{-1}[g/(\text{Pa m})^c]$ and $c=0.15\pm0.02$ for $a_c<1.1\times10^{-2}g$. In equation (4) the errors of b are 2.5% and 0.4% while those of c are 0.5%

and 13%, respectively. With equation (4), the unknown PETFE viscosity of a specimen can be determined by applying a suitable centrifugal acceleration and then measuring the terminal velocity. It should be noted that for $a_c < 1.1 \times 10^{-2} g$, the shallower slope makes the viscosity determination by this method less precise.

RESULTS AND DISCUSSION

Low shear rate viscosity data

A feature of the CBV was that different accelerations, especially low acceleration, could be applied conveniently to measure the terminal velocity of a moving ball in the fluid. At different given applied accelerations, the ball could move at various terminal velocities and thus the shear rate of the ball could be changed. *Figure 2* shows plots of viscosity *versus* shear rate at 280°C for the three PETFE copolymer melts at low shear rate in the Newtonian fluid region. The viscosities of PETFE melts were calculated according to equation (4) and the shear rate ($\dot{\gamma}$) was estimated by using the following relationship[11]:

$$\dot{\gamma} = \frac{4dV_\infty}{D^2 - d^2} \tag{5}$$

where d and D are the diameter of the ball and the i.d. of the sample chamber tube, respectively. The viscosity in the low shear rate limit $\dot{\gamma} \rightarrow 0$, η_0 (zero shear rate viscosity), became a constant, i.e. η is no longer a shear-rate-dependent parameter. *Figure 3* shows a distance *versus* time plot for the TEFZEL 210 sample at 300°C for a time period of about 10000 s at $1.078g$. In such a long time period, the ball moved at a terminal velocity of $4.38 \times 10^{-7}\,\mathrm{m\,s^{-1}}$ and its shear rate was estimated to be 1.77×10^{-6} ($\pm 3 \times 10^{-8}$)$\,\mathrm{s}^{-1}$.

Temperature-dependent viscosity

According to the empirical Arrhenius relationship between viscosity and temperature:

$$\eta = A\,\mathrm{e}^{E_a/RT} \tag{6}$$

where A, E_a, R and T are a proportionality constant, the activation energy ($\mathrm{kcal\,mol^{-1}}$), the gas constant ($1.987\,\mathrm{cal\,mol^{-1}\,K^{-1}}$) and the temperature (K), respectively. *Figure 4* shows the Arrhenius plot of melt viscosities *versus* inverse temperature of the three PETFE copolymers. The solid lines represent the best least-squares fitting of experimental data. The activation energy of different molecular weight PETFE copolymers ranged from 15.0 to 15.5 $\mathrm{kcal\,mol^{-1}}$ (see *Table 3*) with an average E_a, $\langle E_a \rangle$, of 15.3 $\mathrm{kcal\,mol^{-1}}$, which agreed with the values of 6–14.6 $\mathrm{kcal\,mol^{-1}}$ of high density polyethylene/low density polyethylene and 18–36 $\mathrm{kcal\,mol^{-1}}$ of polytetrafluoroethylene (PTFE)[12–15]. The activation energy of PETFE alternating copolymers is essentially independent of molecular weight, as shown in *Figure 5*.

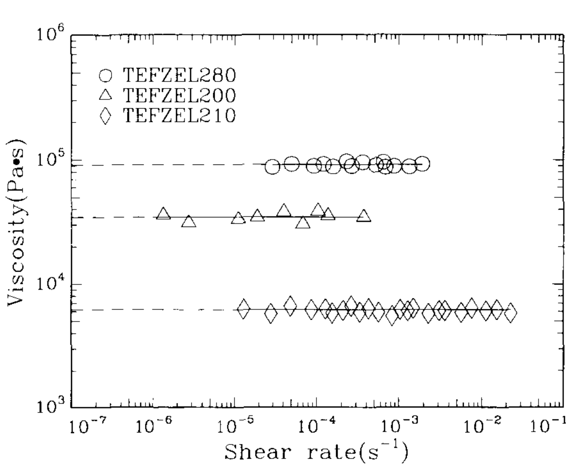

Figure 2 Viscosity *versus* shear rate for three PETFE copolymer melts at 280°C

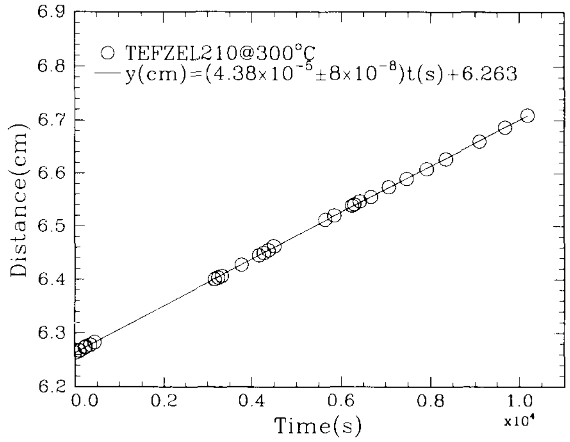

Figure 3 Distance *versus* time plot for TEFZEL 210 copolymer at 300°C

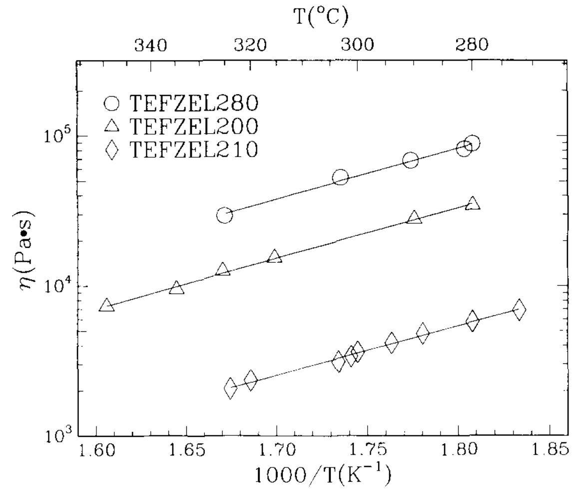

Figure 4 Arrhenius plot of melt viscosities of different molecular weight PETFE copolymer melts

Figure 6 shows a plot of viscosity *versus* molecular weight for PETFE at 280°C from our measurements and those of ref. 6. The relationship between the viscosity and the polymer molecular weight can be described by the well known empirical formula for the polymer with a molecular weight larger than a critical value M_c, $\eta_0 = K(M_w)^{3.43}$, with $K = (1.23 \pm 0.02) \times 10^{-16}$ for our data, while $\eta_0 = K(M_w)^{3.57}$ with $K = (2.00 \pm 0.02) \times 10^{-17}$ for ref. 6. The results agreed quite well to within the experimental error limits, especially when long-chain branching in PETFE, if it exists, has not been taken into account. According to the empirical formula, our results

Table 3 Parameters of Arrhenius equation, $\eta = A\,e^{E_a/RT}$ and $\eta = BM_w^{3.4}\,e^{E_a/RT}$

Samples	E_a (kcal mol^{-1})	A (Pa s)	$B \times 10^{22}$ (Pa s/(g mol^{-1})$^{3.4}$)	$\langle E_a \rangle$* (kcal mol^{-1})	A_1† (Pa s)	$B_1 \times 10^{22}$† (Pa s/(g mol^{-1})$^{3.4}$)
TEFZEL 280	15.5	0.042	1.02	15.3	0.050	1.20
TEFZEL 200	15.4	0.017	0.981	15.3	0.019	1.08
TEFZEL 210	15.0	0.0042	1.36	15.3	0.0032	1.04

* Average value of E_a

† A_1 and B_1 are the fitting values based on the average value $\langle E_a \rangle$ from the Arrhenius equation $\eta = A\,e^{E_a/RT}$ (equation (6)) and $\eta = BM_w^{3.4}\,e^{E_a/RT}$, respectively

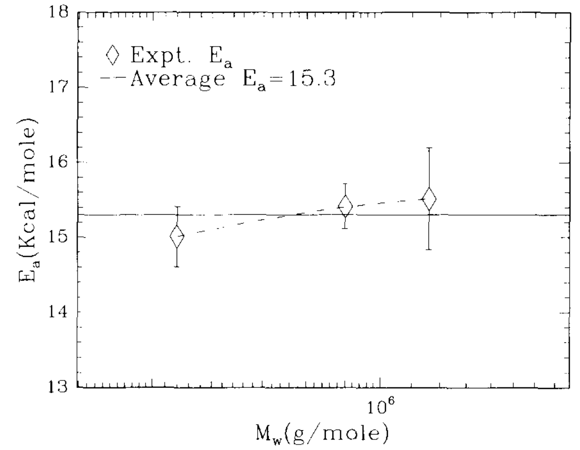

Figure 5 Activation energy of PETFE copolymers with three different molecular weights

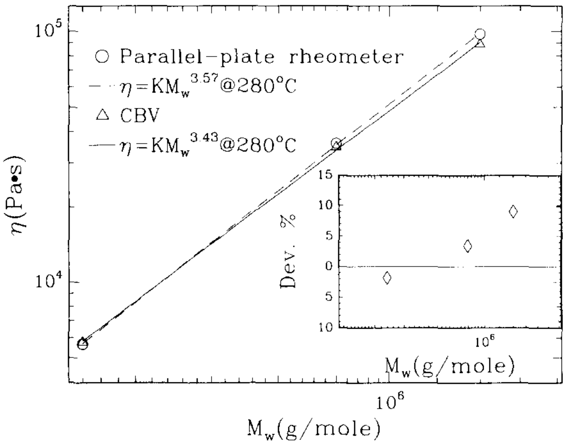

Figure 6 Viscosity of PETFE copolymer melts *versus* molecular weight at 280°C

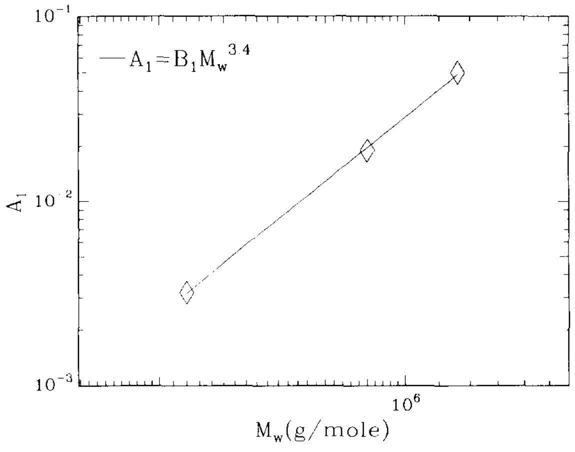

Figure 7 Plot of A_1 *versus* molecular weight of PETFE

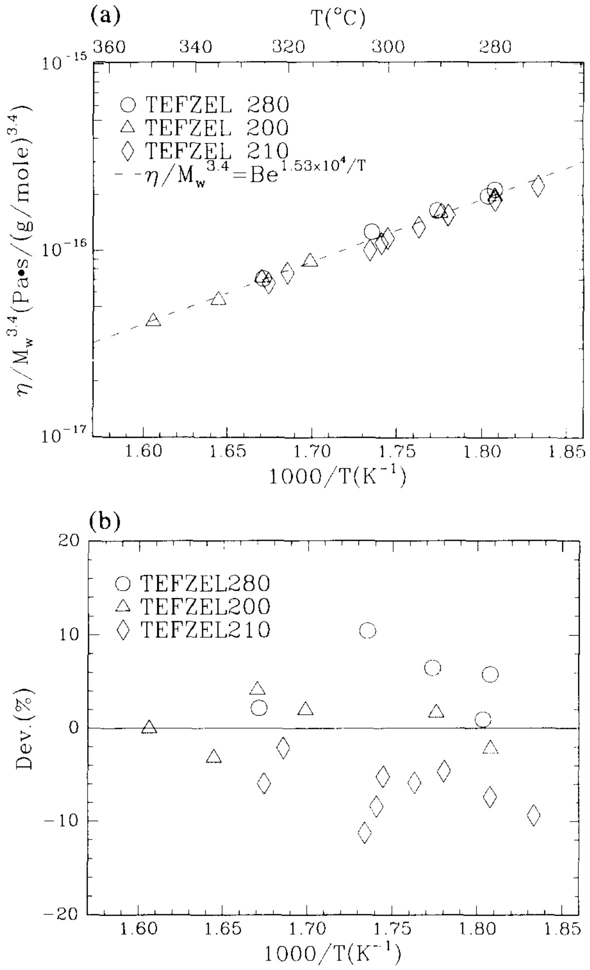

Figure 8 (a) Plot of $\eta/(M_w)^{3.4}$ *versus* $1/T$. Data from all three PETFE copolymers can be plotted on a master curve based on the assumption of the constant activation energy E_a. (b) Deviations (%) = $[\eta/(M_w)^{3.4} - \langle \eta/(M_w)^{3.4} \rangle / \langle \eta/(M_w)^{3.4} \rangle] \times 100$, where angle brackets denote average values

seem closer to the 3.4 power law than those of ref. 6. In ref. 6, the shear rate reached down to $10^{-2}\,s^{-1}$ while the CBV could reach a $\dot{\gamma}$ value down to $10^{-6}\,s^{-1}$. For melt viscosity measurements, the CBV could indeed reach very low shear rates, e.g. $\dot{\gamma} \sim 10^{-8}\,s^{-1}$ is accessible. With well controlled high temperatures, precise distance measurements for the ball movement and extremely low shear rates, the CBV has the capability to determine the zero shear rate viscosity of very high molecular weight polymer melts, to our knowledge more effectively than existing viscometers.

In general, the viscosity of a fluid is dependent on several parameters, such as temperature, pressure, molecular weight and shear rate. The relationships among these variables can be expressed by the following general formula[16-18]:

$$\eta = B(M_w)^{3.4}\, e^{E_a/RT} f(p, \dot{\gamma}) \qquad (7)$$

where B is a proportionality constant and $f(p, \dot{\gamma})$ is a function of pressure and shear rate. At constant pressure and at very low shear rates, equation (7) becomes:

$$\eta = B(M_w)^{3.4}\, e^{E_a/RT} \qquad (8)$$

From equations (6) and (8), we have the relationship between A and B as $A = B(M_w)^{3.4}$. If we assume E_a to be a constant, i.e. if we take the average value of E_a, $\langle E_a \rangle$, with A_1 and B_1 values listed in *Table 3*, then from equations (6) and (8), $A_1 = B_1(M_w)^{3.4}$. *Figure 7* shows a plot of A_1 *versus* the molecular weight of the three PETFE copolymers. The slope B represents the average value of B_1 (see *Table 3*). The B_1 values are all close to that of B since the activation energy E_a is fairly constant.

We can rearrange equation (8) as:

$$\eta/(M_w)^{3.4} = B\, e^{E_a/RT} \qquad (9)$$

Then all the viscosity data for the three different PETFE copolymers measured at different temperatures can be merged into one master curve. *Figure 8a* shows that the data from all three PETFE copolymers can be plotted on a master equation with $E_a = 15.3\,\mathrm{kcal\,mol^{-1}}$ and $B = 1.12 \times 10^{-22}\,\mathrm{Pa\,s/(g\,mol^{-1})^{3.4}}$. *Figure 8b* shows that deviation of all experimental data from equation (9) is acceptably small. From the above discussions, we have established the CBV to be a new technique which can measure the viscosity of PETFE polymer melts at different temperatures and thereby the corresponding molecular weight.

CONCLUSIONS

A newly developed centrifuge ball viscometer has been shown to be a very useful instrument for investigating the zero shear rate viscosity of high molecular weight polymer melts. We measured the viscosity of three different molecular weight copolymers of ethylene and tetrafluoroethylene at various temperatures. The melt viscosity followed the 3.4 power law in molecular weight and $\langle E_a \rangle = 15.3\,\mathrm{kcal\,mol^{-1}}$. Finally, a general relationship among viscosity, molecular weight and temperature for the PETFE copolymers was established: $\eta\ (\mathrm{Pa\,s}) = B(M_w)^{3.4}\, e^{E_a/RT}$, with $B = 1.12 \times 10^{-22}\,\mathrm{Pa\,s/(g\,mol^{-1})^{3.4}}$ and $E_a = 15.3\,\mathrm{kcal\,mol^{-1}}$.

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