Free volume effects on the melt viscosity of low molecular weight poly(methyl methacrylate)

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The zero-shear melt viscosity η_0 has been obtained for a series of low molecular weight PMMA fractions ($M \lesssim 5000$). The strong sensitivity of η_0 to M observed for these fractions is attributed to a depression of viscosity by an M_n-dependent free volume effect. The Rouse model modified with a friction coefficient depending on M_n is shown to describe the data adequately. The necessary free volume parameters were determined from the temperature dependence of viscosity for each fraction through fits to the WLF equation. The influence of the free volume associated with chain ends through the end-group composition is also discussed.

(Keywords: melt viscosity; PMMA; Rouse model; free volume)

INTRODUCTION

The dependence of isothermal melt viscosity on molecular weight for linear polymers is dominated by the onset of entanglement coupling at the so-called critical entanglement molecular weight M_c[1]. M_c is a constant characteristic of a given polymer melt. For molecular weights greater than M_c, the viscosity generally increases with the 3.4 power of molecular weight. Recent experimental evidence[2] indicates an M^3 limiting behaviour at very high molecular weights, in agreement with the prediction based on reptation theory. Experimental observation of the M^3 dependence reconciles the inconsistencies between the 3.4 power law and the observed molecular weight dependences of the recoverable shear compliance, self-diffusion coefficient and radius of gyration[2].

For molecular weights less than M_c, entanglement coupling is not an important factor. The primary contribution to the viscosity is the frictional force experienced by chain segments as they move through the melt. This is expressed by the Rouse model which predicts a first power molecular weight dependence for the melt viscosity[3]. It is not always appreciated, however, that the Rouse model assumes a constant free volume for the melt. This means that the M^1 dependence will only hold in a range of molecular weights less than M_c and greater than the molecular weight for which properties such as specific volume and T_g reach their limiting values. The dependence of specific volume and T_g on molecular weight is attributed to free-volume effects which increase with decreasing molecular weight. This free volume is usually associated with chain ends, whose number per unit volume increases as M^{-1}. It has been shown in the past that free-volume effects influence the melt viscosity as well[3,4]. Various approaches, to be discussed below, have been used to correct for free-volume effects in order to recover the Rouse prediction over the entire range of $M < M_c$. In this paper, we present viscosity data for low molecular weight PMMA fractions which will be modelled in terms of free volume concepts.

THEORETICAL BACKGROUND

Modified Rouse theory

The original Rouse theory for dilute solutions was reformulated by Ferry[5] to apply to undiluted, nonentangled polymers. The zero-shear viscosity η_0 is given by[3]

$$\eta_0 = \frac{\zeta_0 \rho a^2 N_A M}{36 M_0^2} \tag{1}$$

where ζ_0 is the monomeric friction coefficient, ρ is the mass density, a is the equivalent step length, N_A is Avogadro's number, M is the polymer molecular weight and M_0 is the monomer molecular weight. In equation 1, a^2 represents the ratio of the mean-square end-to-end distance to the degree of polymerization. The friction coefficient ζ_0 accounts for the average frictional force per monomer unit experienced by a chain in the shear field. The bulk viscosity η_0 is proportional to the total frictional force and thus to the number of monomer units per chain, or $\eta_0 \sim M$. The temperature dependence of η_0 enters almost entirely through ζ_0, with the small temperature dependence of ρ being negligible. Equation 1 assumes ζ_0 has no molecular weight dependence. In fact, ζ_0 or the quantity η_0/M has been shown many times to increase at low molecular weight and then to reach a limiting value at higher molecular weight still less than M_c (ref. 3). This effect is again attributed to the free volume associated with end groups, and will be discussed in the next section.

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Free volume effects

Equation 1 can be written in the general form

$$\eta_0 = \zeta_0(T,M)F(M) \qquad (2)$$

which represents the product of a friction term ζ_0 and a structure factor F. For nonentangled chains, $F(M)$ is proportional to M. We assume that the molecular weight dependence of ζ_0 is due to variations in the fractional free volume f in the melt. In the free volume theory, the ratio a_T of a mechanical relaxation time at temperature T to its value at a reference temperature T^0 is given by[6]:

$$a_T = \exp[B(1/f - 1/f^0)] \qquad (3)$$

where B is a constant on the order of unity and f and f^0 are the fractional free volumes at temperature T and T^0, respectively. The Rouse relaxation time is proportional to $\eta_0 T\rho$ such that

$$a_T = \frac{\eta_0 T\rho}{\eta_0^0 T^0 \rho^0} \qquad (4)$$

where the zero superscripts denote the reference temperature. The variation of $T\rho$ with temperature is usually neglected in comparison to η_0, such that

$$a_T = \frac{\eta_0(T)}{\eta_0(T^0)} = \exp[B(1/f - 1/f^0)] \qquad (5)$$

a_T generally represents the ratio of a relaxation time in a given state to that in a reference state. If the given state (at molecular weight M) has a fractional free volume f_m and the reference state has a limiting (high molecular weight) free volume f_0, both at the same temperature,

$$\frac{\eta_0(f_m)}{\eta_0(f_0)} = \exp[B(1/f_m - 1/f_0)] \qquad (6)$$

If the fractional free volume increases with the number of chain ends in the same manner as the specific volume[7], then

$$f_m = f_0 + A/M_n \qquad (7)$$

where A is a constant related to the free volume per chain end.

Finally, since the molecular weight dependence of η_0 due to free volume enters only through ζ_0,

$$\frac{\eta_0(f_m)}{\eta_0(f_0)} = \frac{\zeta_0}{\zeta_{00}} \qquad (8)$$

where ζ_{00} represents the monomeric fraction coefficient ζ_0 at sufficiently high molecular weights to neglect chain end effects. Equation 6 then becomes

$$\zeta_0 = \zeta_{00} \exp\left[B\left(\frac{1}{f_0 + A/M_n} - \frac{1}{f_0}\right)\right] \qquad (9)$$

which represents the isothermal variation of ζ_0 with M. Insertion of equation 9 into the Rouse result (equation 1) introduces an additional molecular weight dependence to η_0. This dependence is determined by the number average of the molecular weight distribution and involves the constant A which is proportional to the additional free volume per mole of chain ends.

Returning to equation 5, if f is assumed to increase linearly with temperature between T^0 and T with an expansion coefficient α_f, $f = f^0 + \alpha_f(T - T^0)$ and

$$\log a_T = -\frac{(B/2.303f^0)(T - T^0)}{(f^0/\alpha_f) + T - T^0} \qquad (10)$$

This is the usual derivation of the Williams Landel Ferry (WLF) equation:

$$\log a_T = -\frac{C_1^0(T - T^0)}{C_2^0 + T - T^0} \qquad (11)$$

where $C_1^0 = B/2.303f^0$ and $C_2^0 = f^0/\alpha_f$. Thus, the variation of C_1^0 with molecular weight at a constant reference temperature T^0 can be used to determine the molecular weight dependence of f^0. A M_n^{-1} dependence as in equation 7 is expected.

The theoretical framework described above has been used by other investigators[2,4,8] for low molecular weight polymers. Our approach will be to use the temperature dependence of η_0 at a given molecular weight to obtain f_m, to use the molecular weight dependence of f_m to obtain f_0 and A, and to use independently determined values of ζ_{00} to predict the isothermal viscosities. The full expression for $\eta_0(M)$ is:

$$\eta_0 = \frac{\rho a^2 N_A M}{36 M_0^2} \zeta_{00} \exp\left[B\left(\frac{1}{f_0 + A/M_n} - \frac{1}{f_0}\right)\right] \qquad (12)$$

Colby, Fetters and Graessley[2] took the approach of correcting for free volume effects by multiplying the viscosity values by ζ_{00}/ζ_0 where this quantity was obtained through equations 6 and 8. f_m was calculated from the C_1^0 constant at molecular weight M and f_0 was obtained from C_1^0 at high molecular weight. In this way the M^1 Rouse dependence was recovered for η_0 for a series of polybutadienes. Havlicek and Nicolais[9] have used a configurational entropy approach of the Gibbs–Dimarzio type to describe the melt viscosity of low molecular weight polystyrene.

EXPERIMENTAL

Synthesis and fractionation

The low molecular weight poly(methyl methacrylate) (PMMA) samples used in this study were obtained as follows. A batch of low molecular weight PMMA was first prepared by a high temperature polymerization process[10]. 1200 g of methyl methacrylate (MMA) monomer (99%, Aldrich Chemical, used as received), 26.3 g of ditertiarylbutyl peroxide initiator (Lucidol Inc., used as received) and 300 g of methyl amyl ketone (98%, Aldrich Chemical, used as received) were reacted in a 2000 ml stirred pressure reactor (Parr Instruments model 1522) at 200°C for 90 min. After cooling, the product was dispensed from the reactor. Gravimetric analysis indicated a 52% conversion of monomer to polymer. The relatively low extent of conversion is presumably due to the fact that the reaction was performed close to the 220°C ceiling temperature of MMA[11]. Residual solvent and unreacted monomer were removed with a thin film evaporator. This yielded a clear solid resin exhibiting a $\bar{M}_n$ of 1400, $\bar{M}_w$ of 3370, $\bar{M}_z$ of 16 600, and dispersity ratios of $M_w/M_n = 2.40$ and $M_z/M_n = 11.53$. 47 g of this stripped material were then fractionated according to molecular weight using a supercritical fluid extraction technique described previously[12]. Eight fractions were obtained.

Gel permeation chromatography

Molecular weights were determined by gel permeation chromatography analysis performed at 35°C on a Waters 150C Chromatograph using five μ Styragel columns (1×10^5, 1×10^4, 1×10^3, 500, 100 Å pore sizes) and tetrahydrofuran (THF) as the solvent. The flow rate was 1 ml min^{-1} and 200 μl of a 0.2% solution was injected. The refractive index detector used was the standard unit installed on the Waters chromatograph. Data were acquired and stored on an IBM 9000 computer for subsequent analysis.

Vapour pressure osmometry

Number–average molecular weights were obtained using a Knauer vapour pressure osmometer. Solutions in THF were prepared at concentrations ranging from 5 to 20 g kg^{-1}. Molecular weights were calibrated using a benzil standard.

Differential scanning calorimetry

The glass transition temperatures of the fractions were measured using a DuPont Instruments 9900/910 DSC. T_g was taken as the temperature corresponding to the midpoint of the change in heat capacity associated with T_g. Sample size was 3 to 5 mg. A heating rate of 20°C min^{-1} was used. Temperature offset in the instrument was corrected using a two-point calibration with high-purity water and indium samples.

Melt viscosity

Steady shear melt viscosities were measured with a Rheometrics RDS-7700 Dynamic Spectrometer equipped with 25 mm diameter cone and plate fixtures. Shear rate sweeps from 0.01 to 1.0 s^{-1} were done at a number of different temperatures for each fraction. The data were extrapolated (if necessary) to low shear rate to obtain the zero-shear viscosity at each temperature.

The sample powders obtained from the fractionation process were compression-moulded at $T_g + 60$°C into 25 mm diameter, 1 mm thick discs. They were then annealed under vacuum at $T_g + 60$°C to remove any residual gas bubbles. The samples were installed in the test fixtures, brought to temperature and trimmed to size. All tests were conducted under a dry N_2 atmosphere. Thermal expansion of the test fixtures was accounted for in order to maintain a constant gap of 0.05 mm between the cone and plate.

RESULTS AND DISCUSSION

Molecular weight characterization

Values of M_n, M_w and M_z for the fractions are shown in *Table 1*. These values were obtained from GPC and represent polystyrene-equivalent molecular weights since the calibration curve of molecular weight *versus* elution volume was established using polystyrene standards. Values of M_w/M_n and M_z/M_n are fairly constant at about 1.3 and 1.6, respectively, for the first seven fractions. Fraction 8 was not included in the series for viscosity measurements because of its broad molecular weight distribution. Also shown in *Table 1* are the absolute M_n values determined by VPO. It is seen that the VPO values for M_n are approximately 10% higher than those from GPC. This indicates that the hydrodynamic volume of PMMA in THF is about 10% smaller than polystyrene of equal molecular weight, in the low molecular weight range of interest here. Part of the difference can be attributed to polystyrene having 4% more mass per unit repeat length than PMMA (104 compared to 100 for the monomer molecular weights). In the remainder of this paper, the VPO results will be taken as the true M_n, and the GPC results will be taken to provide a reasonable estimate of M_w/M_n.

Table 1 Molecular weight characterization

Fraction	GPC					VPO
no.	M_n	M_w	M_z	M_w/M_n	M_z/M_w	M_n
1	680	880	1090	1.29	1.60	760
2	800	1070	1340	1.34	1.67	900
3	1160	1500	1830	1.29	1.58	1230
4	1420	1870	2250	1.32	1.58	1580
5	1790	2250	2960	1.26	1.65	2210
6	2340	2940	3380	1.26	1.44	2600
7	4930	6310	9890	1.28	2.00	5580
8[a]	9970	43190	78730	4.33	7.90	–

[a] Not used for viscosity measurements

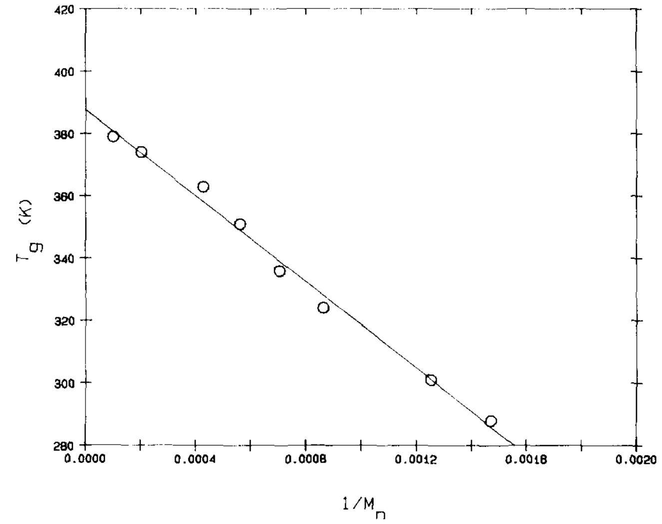

Figure 1 Glass transition temperature T_g as a function of $1/M_n$ for the PMMA fractions, yielding $T_{g(\infty)} = 114.7$°C and $K = 0.69 \times 10^5$

Glass transition temperatures

The effect of molecular weight on T_g is shown in *Figure 1*. The data are described by the classical chain-end relation[13]:

$$T_g = T_{g(\infty)} - K/M_n \tag{13}$$

where $T_{g(\infty)}$ is the T_g at infinite molecular weight and $K = 2\rho N_A \theta/\alpha_f$, where θ is the free volume per chain end and the remaining quantities are as defined previously. A linear least squares fit of the data yields $T_{g(\infty)} = (114.7 \pm 2.1)$°C and $K = (0.691 \pm 0.025) \times 10^5$ where the error limits denote one standard deviation. $T_{g(\infty)}$ values for PMMA have been shown to be strongly influenced by tacticity[14]. The value of 115°C obtained in this study is consistent with an atactic microstructure[14,15]. Only limited data exists in the literature on the molecular weight dependence of T_g for atactic PMMA. Thompson[14] reported a $T_{g(\infty)}=114.2$°C and $K=2.95\times10^5$ for an atactic PMMA series prepared by electron irradiation of a high molecular weight sample. Since the value of K is dependent on the structure of the chain ends (through θ), differences in K between our results and Thompson's are attributed to different chain-end composition. It is also noted that the lowest molecular weight sample in Thompson's series had $M_n=13\,000$, and thus his data span a different part of the T_g *versus* M_n behaviour than ours.

Shear rate dependence of viscosity

For the series of PMMA fractions studied, there was no discernible dependence of the melt viscosity η on the shear rate $\dot{\gamma}$. This is an expected result since all molecular weights are well below the M_c of 30000 for PMMA[1] so that non-Newtonian shear thinning associated with entanglements is absent. Representative data are shown in *Figure 2* for fraction 4 at a series of different temperatures. Extrapolations to zero-shear rate were not necessary to establish the zero-shear viscosity η_0.

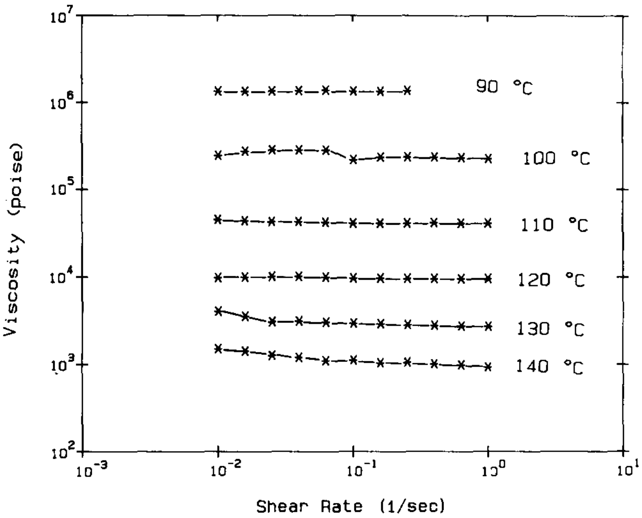

Figure 2 Melt viscosity η *versus* shear rate $\dot{\gamma}$ for fraction 4 at different temperatures, showing Newtonian flow behaviour

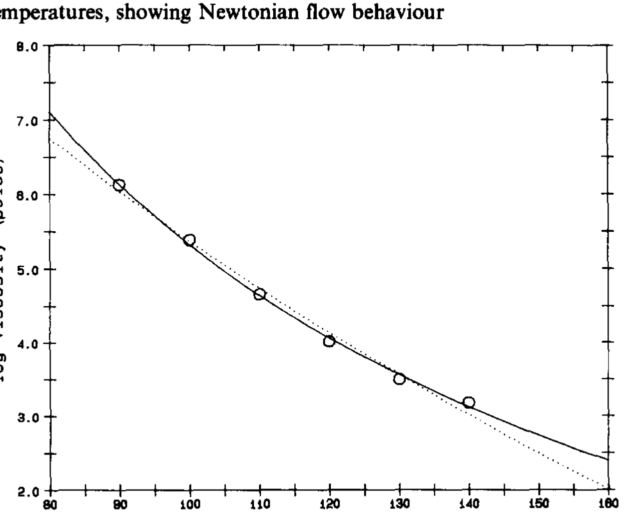

Figure 3 Log viscosity *versus* temperature for fraction 4. Solid line: fit to equation 15 (WLF). Dotted line: fit to equation 14 (Arrhenius)

Table 2 WLF parameters at 120°C from temperature dependence of viscosity

Fraction no.	C_1	C_2 (deg)
1	4.72±0.53	172.2±7.6
2	5.29±0.23	161.9±3.8
3	8.19±4.67	224.3±73.0
4	6.02±1.14	113.3±17.0
5	6.68±0.61	96.3±9.5
6	6.29±0.52	86.4±4.5
7	9.05±1.08	85.1±19.5

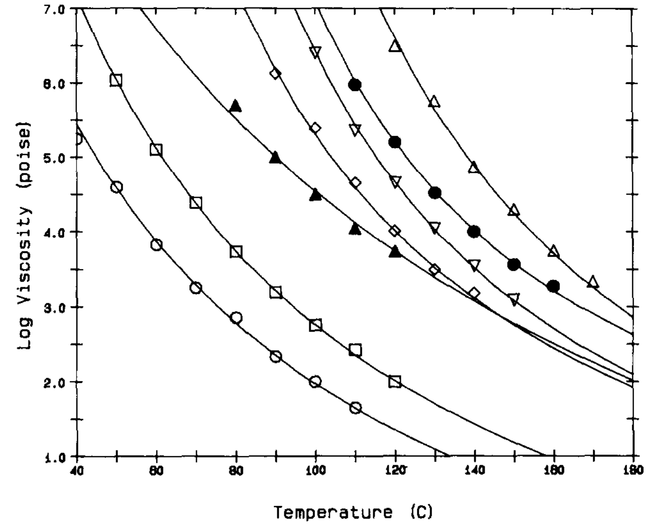

Figure 4 Log viscosity *versus* temperature for PMMA fractions. Solid lines represent fits to the WLF equation. The molecular weight of the fractions increases from the lower left to upper right in the graph

Temperature dependence of viscosity

There are several commonly used equations to describe the temperature dependence of η_0, including the Arrhenius form

$$\ln\eta_0=\ln A-E_a/RT \tag{14}$$

where A is a constant, E_a is an activation energy, and R is the gas constant and the WLF form described above

$$\ln\eta_0=\ln\eta_0(T^0)-\frac{2.303\,C_1^0(T-T^0)}{C_2^0+T-T^0} \tag{15}$$

Representative viscosity temperature data are shown in *Figure 3* for fraction 4. It can be seen that the fit to the WLF equation is excellent over the temperature range investigated whereas the Arrhenius equation gives a poor fit. The latter result is expected since the range of applicability of the Arrhenius equation to polymer melt viscosity is often quoted as $T>T_g+100$°C[3]. *Table 2* shows the results of the WLF fits, where the reference temperature T_0 was chosen as 120°C and C_1 and C_2 were taken to be fitting parameters. The errors associated with the values reported in *Table 2* represent ±3 standard deviations. *Figure 4* shows the WLF plots for all the fractions.

Molecular weight dependence of viscosity

When plotted at constant temperature, the melt viscosities of the fractions are much more sensitive to molecular weight than the Rouse prediction (equation 1).

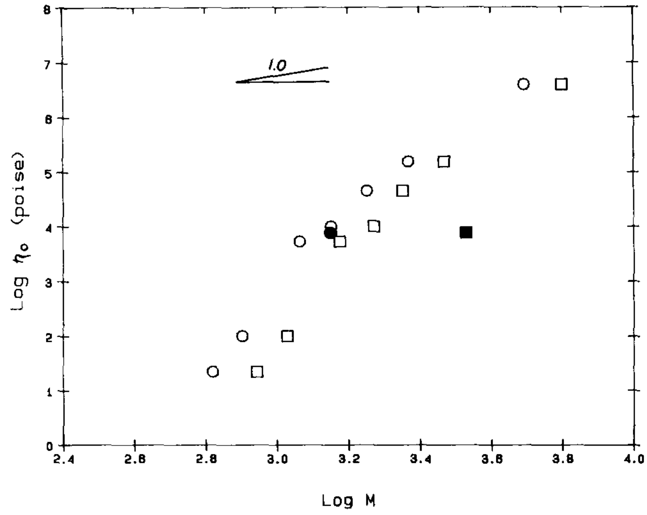

Figure 5 Log–log plot of zero-shear viscosity η_0 *versus* molecular weight at 120°C in terms of M_n and M_w. ○ = M_n of fractions; ● = M_n of parent polymer; □ = M_w of fractions; ■ = M_w of parent polymer. A slope of 1.0 is shown for comparison

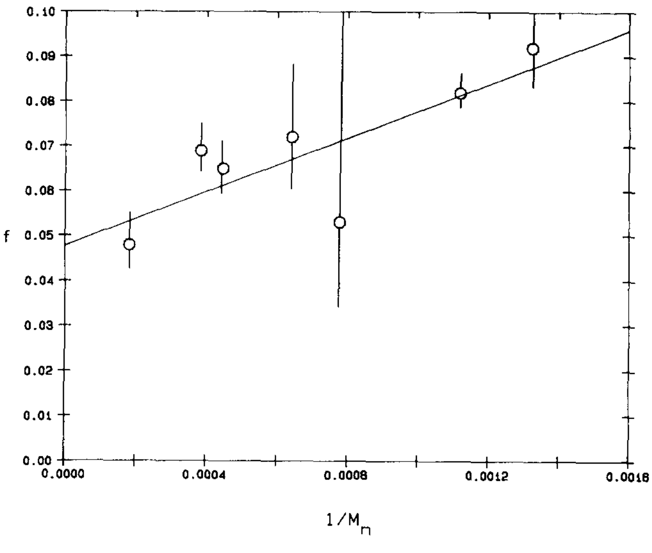

Figure 6 Plot of fractional free volume f at 120°C *versus* $1/M_n$. The slope and intercept yield $A = 30.1$ and $f_0 = 0.047$. Error bars represent error limits on C_1 from *Table 3*

Figure 5 shows a plot of $\log \eta_0$ *versus* $\log M$ for the fractions at 120°C. The data are plotted in terms of both M_n and M_w (GPC values) for the fractions. The data lie on approximately parallel curves because of the nearly constant M_w/M_n values for each fraction. The data are not described by a line having a slope of one, which is the Rouse prediction. Rather, the data lie on a curve which has a limiting slope of approximately 8 at low molecular weight. It is also seen from *Figure 5* that the zero-shear viscosity of the parent (unfractionated) polymer correlates more closely with the fractions in terms of its M_n rather than its M_w. It is well known that η_0 correlates with M_w or higher moments of the molecular weight distribution for both entangled and nonentangled polydisperse polymers[3,8,16]. Both the sensitivity of η_0 to M and its correlation with M_n are related to the free volume effects discussed above. In the next section, we will attempt to fit the data of *Figure 5* in terms of free volume.

Free volume model

Here we describe the data of *Figure 5* in terms of a free volume model such as described by equation 12. The values of f_0 and A were obtained from the molecular weight dependence of f according to equation 7. *Figure 6* shows a plot of f *versus* $1/M_n$ at 120°C where f was obtained from the WLF fits to the viscosity–temperature data for each fraction. f was calculated from $f = B/2.303C_1^0$ with B taken to be unity and C_1^0 obtained at a reference temperature of 120°C. M_n values were taken from VPO. A linear least-squares fit to *Figure 6* yields $f_0 = 0.047$ and $A = 30.1$. Values of ζ_{00} have been tabulated by Ferry[3] for a number of different polymers. Values for atactic PMMA are available from this source over a temperature range which encompasses 120°C. For purposes of interpolation to obtain ζ_{00} at 120°C, the data were linearized by plotting $\log \zeta_{00}$ *versus* $1/(T - T_\infty)$ where $T_\infty = 96.5$°C. A value of $\log \zeta_{00} = -0.56$ (dynes s cm^{-1}) was obtained. The other quantities required by equation 12 were taken as $a = 6.9 \times 10^{-8}$ cm, $M_0 = 100$ g/mol, and $\rho = 1.12$ g/cm^3. The relatively small molecular weight dependence of ρ in the pre-exponential term was neglected in comparison to the exponential term.

Figure 7 shows a plot of $\log \eta_0$ *versus* $\log M_n$ for the experimental data at 120°C. The curve calculated according to equation 12 is also shown. It is seen that equation 12 with the free-volume parameters determined as described above describes both the magnitudes of η_0 and the form of its dependence on M_n reasonably well. The experimental viscosities for the two lowest M fractions fall significantly below the prediction of equation 12.

The value of f_0 obtained from the WLF fits and its influence on the form of $\eta_0(M)$ require further examination. The constant B appearing in equations 3, 9 and 12 has been taken as unity. More correctly, the WLF C_1 parameter yields f/B rather than f. Our extrapolation of the f/B values of the fractions to high molecular weight gave $f_0/B = 0.047$ at 120°C. A value of 0.013 has been measured for f/B for atactic PMMA at its T_g[16]. It is also of interest to examine the fractional free volumes of the fractions at their respective T_g. This is accomplished

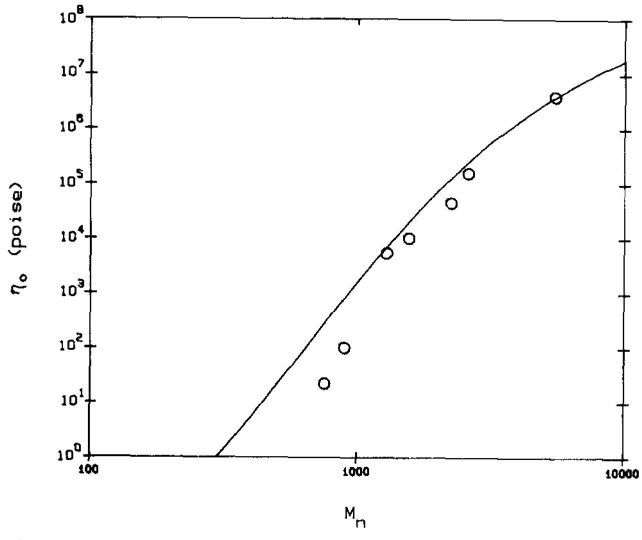

Figure 7 Log η_0 *versus* log M_n at 120°C. The points are the experimental data. The line is calculated from equation 12 using parameters calculated as described in the text

Table 3 Fractional free volumes at T_g

Fraction no.	T_g (*K*)	f_g/B
1	288	0.036
2	301	0.035
3	324	0.037
4	336	0.036
5	351	0.037
6	363	0.045
7	374	0.037

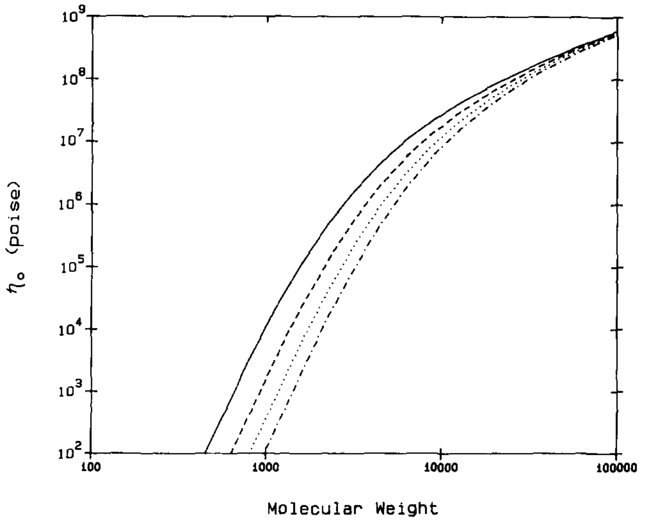

Figure 8 Curves of log η_0 *versus* log M_n calculated for various values of A with $f_0=0.047$ and $\log\zeta_\infty=-0.56$. (——) $A=20$; (– – –) $A=30$; (·····) $A=40$; (–·–·–) $A=50$

through the following relation[3]:

$$f_g/B=(C_2^0+T_g-T^0)/2.303\,C_1^0\,C_2^0 \qquad (16)$$

where the subscript 'g' denotes the glass transition temperature. *Table 3* shows the values of f_g/B for the fractions. With the exception of fraction 6, the values are all approximately 0.036 and show no trend with molecular weight. Part of the discrepancy between our f_g/B values and the accepted value for atactic PMMA is attributed to the method of T_g determination. Our DSC method using a finite heating rate does not represent a quasi-static or near-equilibrium determination such as achieved using dilatometry, for example.

One can also improve the fit to the data of *Figure 7* by treating A and f_0 as independent fitting parameters and using a non-linear least squares approach. This approach was not pursued because it ignores the functional relationship between A and f_0 expressed by equation 7. We prefer to consider the deviation of our calculated curve in *Figure 7* from the experimental data at the lowest molecular weights as perhaps being due to limitations in the Rouse model. Equation 1 and in turn, the pre-exponential of equation 12, originate from a bead-spring model involving the end-to-end distances of Gaussian submolecules within a random coil[17]. The validity of the submolecule concept as well as the assumed Gaussian chain statistics may be questioned at the lowest molecular weights.

The effect of the parameter A on the η_0 *versus* M behaviour is of interest, since A is presumed to be proportional to the free volume per chain end and thus is influenced by chain-end composition. *Figure 8* shows η_0 *versus* M behaviour calculated for different values of A for PMMA, assuming $\log\zeta_0=-0.56$ and $f_0=0.047$. It is seen that, for the lower molecular weights, η_0 can be depressed by an order of magnitude or more when A changes from 20 to 50, for example. We are currently pursuing this chain-end effect experimentally. *Figure 8* obviously assumes that A can be varied independently of f_0, which may not be possible experimentally.

We have not addressed the effects of polydispersity. The data of *Figure 5* properly suggest that the free volume effect is governed by M_n for a polydisperse polymer. However, the M which appears in the Rouse equation (equation 1) and in the pre-exponential of equation 12, should be the M_w of the distribution, since free volume is assumed to be constant. For our fractions, the M_w/M_n values are approximately constant at 1.3, so the choice of M_n rather than M_w in the pre-exponential represents only a slight vertical shift on a log η_0 scale.

CONCLUSIONS

The isothermal melt viscosity of low molecular weight PMMA fractions was successfully described by the Rouse model modified for free volume. The parameters required to describe the molecular weight dependence were obtained from the WLF description of the temperature dependence of viscosity for each fraction. This free volume approach predicts both the magnitude of the viscosity and its high sensitivity to molecular weight.

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