

Relationship between Molecular Structure and Zero-Shear Viscosity of Polymers

TAKESHI YAMAMOTO,¹ HIROAKI FURUKAWA²

¹ TOSOH Analysis and Research Center, 1-8 Kasumi, Yokkaichi, Mie 510-8540, Japan

² Yokkaichi Laboratory, TOSOH Corporation, 1-8 Kasumi, Yokkaichi, Mie 510-8540, Japan

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ABSTRACT: The relationship between molecular structure and zero-shear viscosity of polymers was studied. In this study we propose a new equation, which is based on Berry and Fox's equation. This new equation is constructed from some molecular parameters, such as mean square length and average molecular weight of statistical skeletal unit, characteristic ratio, entanglement molecular weight, glass-transition temperature, free volume fraction at glass-transition temperature, and thermal expansion coefficient of free volume. It is proposed that some of these molecular parameters could be predicted by group contribution methods, except for the free volume parameters. We also propose new empirical relations between free volume parameters and molecular structures of polymers, which make it possible for free volume parameters to be obtained from molecular structure. Using these relationships, it is possible that the zero-shear viscosity and its temperature dependence are obtainable from the molecular structure of polymers. We applied this formula to some polymers, including both amorphous and semicrystalline polymers. Comparison between the measured and calculated zero-shear viscosity showed quite good agreement. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1609–1618, 2001

Key words: zero-shear viscosity; group contribution method; free volume

INTRODUCTION

We set out to determine the relationships between fundamental properties and valuable properties for practical use. Previously we reported that the deformation-fracture properties of glassy polymers, such as shear yield stress and crazing stress, could be expressed by some molecular parameters.^{1,2} Shear yield stress is represented by characteristic ratio, cohesive energy density, glass transition temperature, and size of the ef-

fective moving unit. Crazing stress is represented by surface free energy, entanglement density, entanglement mesh size, bond energy, and shear yield stress. These molecular parameters can be obtained from the chemical structure of polymers by using group contribution methods.^{3–6} It is thus also possible to calculate both shear yield stress and crazing stress.⁶

In this study we propose a new relationship between zero-shear viscosity and structure of polymers. Zero-shear viscosity is one of the rheological properties of polymer melt that are related to the processability. The relationship between molecular structure and zero-shear viscosity of polymers was reported by Berry and Fox.⁷ In their report zero-shear viscosity was represented

Correspondence to: T. Yamamoto (yamamototakesi@tosoh-arc.co.jp).

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by mean square radius of gyration, entanglement molecular weight, free volume, and so on. We transformed their equation to a more simple form. It is constructed from some molecular parameters, such as mean square length and average molecular weight of statistical skeletal unit, characteristic ratio, entanglement molecular weight, glass-transition temperature, free volume fraction at glass-transition temperature, and thermal expansion coefficient of free volume. If these molecular parameters can be obtained from the molecular structure, we can predict the zero-shear viscosity. It was previously reported that glass-transition temperature, characteristic ratio, and entanglement molecular weight could be obtained by group contribution methods.^{3,5} However, the relationships on free volume parameters are not known. We proposed to examine the relationships between free volume parameters and molecular structure of polymers, to establish new empirical relationships.

We then planned to calculate zero-shear viscosity of some polymers with various molecular weights and at various temperatures, and to compare calculated values and experimental ones.

EXPERIMENTAL

The measurements of the linear dynamic viscoelasticity were made by using a rheometer (MR-500; Rheology Co., Muko City, Kyoto, Japan). The parallel plate geometry was used with a diameter of 20 mm and a gap separation of about 1 mm. Dynamic viscosity was determined in the frequency range between 10^{-3} and 1 Hz at various temperatures, under nitrogen atmosphere. After measurement at the highest testing temperature, a measurement at a lower temperature was repeated to confirm the absence of thermal degradation. The dynamic viscosity showed the constant value in the lower frequency range, which was considered to be the zero-shear viscosity. The entanglement molecular weight was obtained from the plateau modulus,^{2,8} and then C_∞ was calculated by using the relationship proposed by Wu.⁸

Time-temperature superposition was done by horizontal shift, and the shift factor $a_T(T)$ was obtained. From the temperature dependence of the shift factor, the free volume parameters, such as free volume fraction at glass-transition temperature f_g and thermal expansion coefficient α_f

were calculated according to the best fit to the next equation⁹:

$$\log(a_T) = -\frac{\alpha_f(T - T_g)}{2.303f_g} \left[\frac{B}{f_g + \alpha_f(T - T_g)} \right] \quad (1)$$

where T and T_g are testing temperature and glass-transition temperature, respectively. B is a constant and usually equals 1.^{7,9}

Glass-transition temperatures were measured by differential scanning calorimetry (DSC) by use of a Perkin-Elmer calorimeter DSC-7 (Perkin-Elmer, Foster City, CA). A sample, of about 10 mg weight, sealed in the aluminum pan was used for the measurement. It was heated from room temperature at a scanning rate of 10 K/min under nitrogen atmosphere. The glass-transition temperature was taken to be the middle point in the transition.

RESULTS AND DISCUSSION

Equation of Berry and Fox

The relationship between zero-shear viscosity and structure of polymers was reported by Berry and Fox.⁷ It is represented by the following equations:

$$\eta_0 = F(X)\zeta(\rho) \quad (2)$$

$$F(X) = \frac{N_A}{6} X_C \left(\frac{X}{X_C} \right)^a \quad (3)$$

$$X = g \frac{\langle s^2 \rangle}{M} Z \frac{\varphi_2}{v_2} \quad (4)$$

$$\zeta(\rho) = \zeta_{00} \exp\left(\frac{W}{T}\right) \exp\left[\frac{B}{f_g + \alpha_f(T - T_g)} \right] \quad (5)$$

where N_A is Avogadro's number, $\langle s^2 \rangle$ is the mean square radius of gyration, g is the ratio between $\langle s^2 \rangle$ of branched and linear polymer with the same molecular weight, Z is the number of the statistical skeletal bond of the polymer chain with molecular weight M , so Z equals M/m_v , where m_v is the molecular weight of the statistical skeletal bond. The statistical skeletal bond is a minimum movable unit by free rotation around its backbone axis.^{5,8} v_2 is the polymer-specific volume; φ_2 is the volume fraction of polymer; X_C is X

Table I Measurement Molecular Parameters

	$\langle l_v^2 \rangle$ (Å)	m_v (g/mol)	C_∞	M_e (g/mol)	T_g (K)	f_g	$\alpha_f \times 10^4$ (K ⁻¹)
Polystyrene	2.34	52	10.3	20,000	373	0.033	6.9
Polycarbonate of bisphenol A	43.7	127	2.5	2100	423	0.043	7.7

with the critical molecular weight M_c , which is about twofold the entanglement molecular weight M_e . When M is larger than M_c , $a = 3.4$; when M is smaller than M_c , then $a = 1$. ζ_{00} is the limiting friction factor at infinite temperature; W is an additive factor, and usually $\exp(W/T) = 1$; B is the free volume parameter, giving the fractional critical volume required for segmental motion, and usually equals 1; f_g is the free volume fraction at glass-transition temperature T_g ; α_f is the thermal expansion coefficient of free volume; and T is the testing temperature.

Berry and Fox represent the very simple expression in their report.⁷ They made some assumptions and used the average values of mainly vinyl polymers for the molecular parameters, and then they derived the following equation from eqs. (2)–(5).

$$\log \eta_0 = a \log \left(\frac{g\varphi_2 Z}{m_v} \right) - 1.1(a - 1) - 4.1 + \frac{1000}{57.5 + T - T_g} \quad (6)$$

In this study we suppose that the following system is considered. The molecular weight of polymer is much higher than M_c , so $a = 3.4$. Only a linear polymer is considered, so $g = 1$. Solvent, plasticizer, and diluent are not included, so $\varphi_2 = 1$. Equation (6) is then transformed to

$$\log \eta_0 = 3.4 \log \left(\frac{Z}{m_v} \right) - 6.74 + \frac{1000}{57.5 + T - T_g} \quad (7)$$

In this equation, the character of each polymer is represented by only two parameters, average molecular weight of statistical skeletal unit m_v and glass-transition temperature T_g . When we substitute these two molecular parameters and give testing temperature T and molecular weight M ($=Zm_v$), we can calculate the zero-shear viscosity.

The zero-shear viscosity and its temperature dependence were calculated by eq. (7). The molecular parameters used in the calculations were measured values, as listed in Table I. Calculated values were compared with the measured values in Figures 1 and 2 for polystyrenes and polycarbonates, respectively. It is clear that it is impossible to predict the zero-shear viscosity from eq. (7) because values of molecular parameters are too different from those of average parameters and eq. (7) was derived by using these average values.

Modified Equation

We set out to derive a new equation with fewer assumptions for the molecular parameters. Some molecular parameters were converted by using well-known relations as follows.

The relationship between mean square radius of gyration $\langle s^2 \rangle$ and mean square end-to-end distance $\langle R^2 \rangle$ is represented by¹⁰

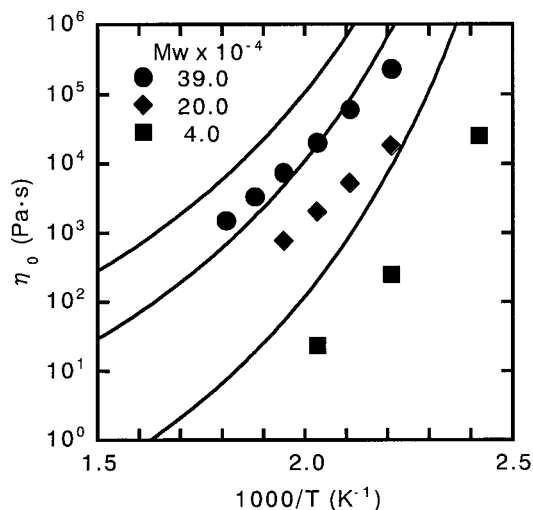


Figure 1 Comparison between the calculated and measured values of zero-shear viscosity of polystyrenes with various molecular weights. The solid lines are calculated values and the symbols are measured values. Calculated values are obtained by using eq. (7).

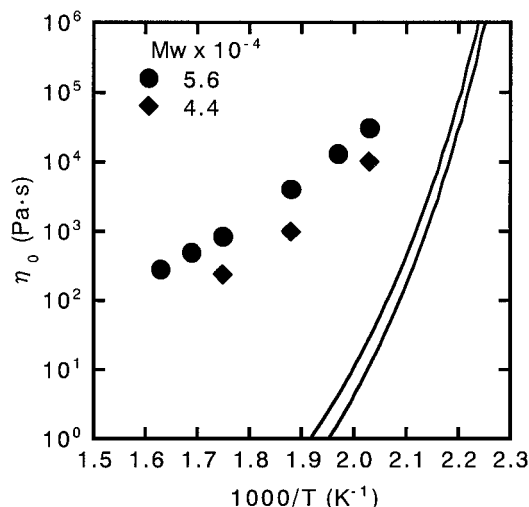


Figure 2 Comparison between the calculated and measured values of zero-shear viscosity of polycarbonates with various molecular weights. The solid lines are calculated values and the symbols are measured values. Calculated values are obtained by using eq. (7).

$$\langle s^2 \rangle = \frac{\langle R^2 \rangle}{6} \quad (8)$$

$\langle R^2 \rangle$ can be represented by^{8,10}

$$\langle R^2 \rangle = C_\infty Z \langle l_V^2 \rangle \quad (9)$$

and Z_C is^{5,8}

$$Z_C = 2Z_e = 6C_\infty^2 \quad (10)$$

where C_∞ is the characteristic ratio, Z is the number of statistical skeletal bond and equals M/m_V , where M is the molecular weight of polymer and m_V is the molecular weight of statistical skeletal bond, $\langle l_V^2 \rangle$ is the mean square length of the statistical skeletal bond, respectively. Z_C is Z at the critical molecular weight, which is equal to $2Z_e$, where Z_e is Z at the entanglement molecular weight.

ζ_{00} , W , B , φ_2 , and v_2 are assumed to be constants, as did Berry and Fox.⁷ $\log \zeta_{00} = -10.6$, $\exp(W/T) = 1$, $B = 1$, $\varphi_2 = 1$, and $v_2 = 1$, respectively.

We substituted these relations in eqs. (2)–(5), then we obtained the next equation (see Appendix):

$$\log \eta_0 = \log\left(\frac{N_A}{6}\right) + \log\left(\frac{C_\infty^3 \langle l_V^2 \rangle}{m_V}\right) + 3.4 \log\left(\frac{M_w}{2M_e}\right) + \log \zeta(\rho) \quad (11)$$

$$\log \zeta(\rho) = -10.6 + \frac{1}{2.303} \left[\frac{1}{f_g + \alpha_f(T - T_g)} \right] \quad (12)$$

The first term of the right hand side of eq. (11) is a constant, and the second, third, and fourth terms are related to molecular stiffness, molecular weight, and temperature dependence of free volume, respectively. When these molecular parameters are known, one can derive the zero-shear viscosity from this equation as described below.

Group Contribution Methods

By using modified eqs. (11) and (12), it is possible to predict zero-shear viscosity from some molecular parameters, such as mean square length and average molecular weight of statistical skeletal unit, characteristic ratio, entanglement molecular weight, glass-transition temperature, free volume fraction at glass-transition temperature, and thermal expansion coefficient of free volume.

The mean square length of the statistical skeletal unit is easily obtained from the molecular structure of polymer.⁵ The average molecular weight of the statistical skeletal unit is the quotient of the molecular weight of the repeat unit divided by the number of statistical skeletal unit in the repeat unit. It was previously reported that the characteristic ratio,⁵ entanglement molecular

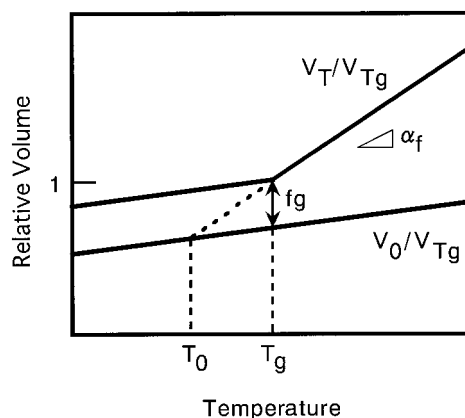


Figure 3 Schematic variation of observed volume and free volume with temperature.

Table II Free Volume Fraction f_g and Thermal Expansion Coefficient α_f

	T_g (K)	f_g	$\alpha_f \times 10^4$ (K ⁻¹)	T_0 (K)
Polyisobutylene ^a	205	0.031	4.4	135
Poly(vinyl acetate) ^a	305	0.028	5.9	258
Poly(vinyl chloroacetate) ^a	296	0.025	6.2	256
Polystyrene ^{a,b}	373	0.033	6.9	325
Poly(α -methylstyrene) ^a	445	0.032	6.4	395
Poly(methyl acrylate) ^a	276	0.024	5.3	231
Polyhexene ^a	218	0.025	5.0	168
Poly(acetaldehyde) ^a	243	0.030	12.5	219
Poly(2,6-dimethyl-1,4-phenylene oxide) ^a	198	0.027	11.3	175
Poly(methyl methacrylate) ^a	378	0.021	3.6	320
Poly(ethyl methacrylate) ^a	335	0.025	3.7	267
Poly(<i>n</i> -butyl methacrylate) ^a	300	0.026	2.6	200
Poly(<i>n</i> -hexyl methacrylate) ^a	268	0.025	1.9	136
Poly(<i>n</i> -octyl methacrylate) ^a	253	0.027	2.5	145
Poly(ethyl hexyl methacrylate) ^a	284	0.021	1.8	167
Polycarbonate of bisphenol A ^{a,b}	423	0.043	7.7	367
Polysulfone ^b	463	0.040	5.9	395
Poly(ether sulfone) ^b	498	0.049	6.3	420
Phenoxy resin ^b	370	0.049	8.3	311
Polyarylate ^b	463	0.043	8.3	411

^a Cited from Ref. 9.^b Measurement values by authors.

weight,⁵ and glass-transition temperature³ could be obtained from the molecular structure by group contribution methods. However, the relationships between molecular structure and free volume parameters f_g and α_f are not known.

The schematic variation of volume with temperature⁹ is shown in Figure 3, and the free volume fraction at a temperature T is expressed by

$$f(T) = f_g + \alpha_f(T - T_g) \quad (13)$$

where $f(T)$ is free volume fraction at temperature T .

It has been assumed that f_g and α_f have constant values, regardless of the structure of polymers. According to the universal WLF equation, f_g and α_f are 0.025 and 4.8×10^{-4} , respectively. However, it was previously reported that they are dependent on the structure of polymers,⁹ as shown in Table II. We propose new semiempirical relationships between the free volume parameters and the structure of polymers, as described below.

The free volume is simply considered to be the difference between the observed and occupied volume. When the van der Waals volume is consid-

ered in relation to the occupied volume, the value of the free volume fraction is much greater than the measurement value, for example, polystyrene at about 0.25.

Some other concepts of free volume were previously proposed, one of which is the fluctuation volume, proposed by Bondii.¹¹ We found that the free volume of polymer could be predicted by using this model. The fluctuation volume is the volume swept out by the center of gravity of the molecule as the result of its thermal vibration. For polymer, we considered an atomic group, which is the minimum movable unit, instead of one molecule. In this concept, the free volume is represented by the following. It is assumed that each atomic group is a sphere and has the van der Waals volume. Then the region where the center of each atomic group can move (shown in Fig. 4) can be represented by

$$V_f = \frac{4\pi}{3} \left(\frac{V_T - V_w}{A} \right)^3 \quad (14)$$

$$f_g = \frac{V_f(T_g)}{V_T(T_g)} \quad (15)$$

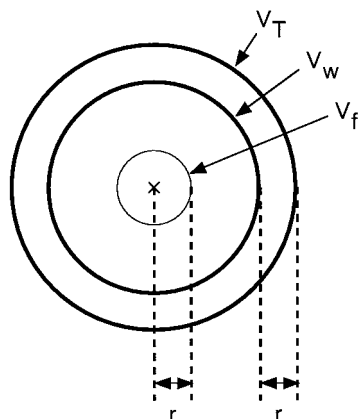


Figure 4 Schematic diagram of fluctuation volume. Fluctuation volume is represented by volume swept out by the center of gravity of one atomic group as the result of its thermal vibration. V_w , V_T , and V_f are van der Waals volume, observed volume, and fluctuation volume, respectively.

where V_f is the fluctuation volume, V_T is the observed volume at temperature T , V_w is the van der Waals volume, and A is the surface area of van der Waals volume, except for the overlapping area with neighboring atomic groups. The van der Waals volume and its surface area can be obtained from the geometry of polymer, and the observed volume can be obtained from the chemical structure of polymer by the group contribution method.³ However, the shape of the atomic group of the van der Waals volume is not actually

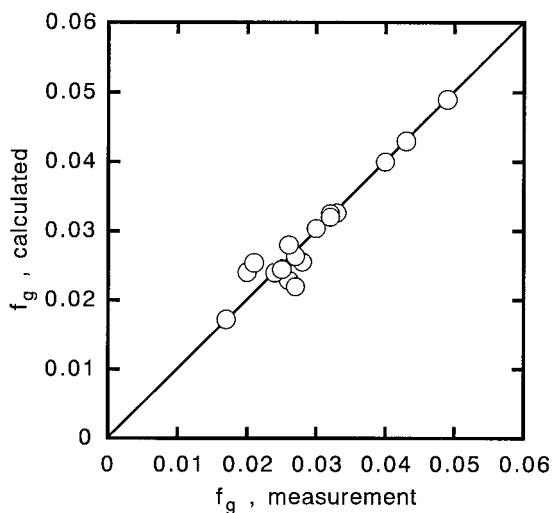


Figure 5 Comparison between the calculated and measured values of f_g . Calculated values are obtained by using eqs. (14) and (15).

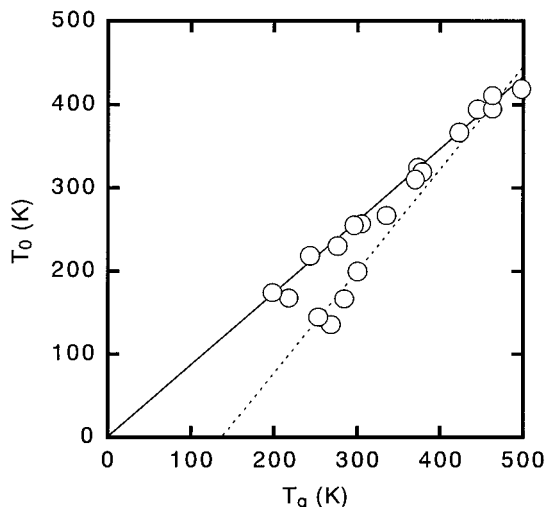


Figure 6 T_0 versus T_g . T_0 are calculated from f_g and α_f according to eq. (13). The solid line is for the polymers without side branch and the dotted line is for the polymers with side branch.

a sphere, so the parameters of surface area in this group contribution method were considered to be adjustable parameters and we optimized them. As shown in Figure 5, the free volume fractions obtained by this way are in agreement with those of the free volume, which are decided by the WLF formula.

The other free volume parameter is the thermal expansion coefficient of free volume α_f . Assuming that the free volume changes in α_f with temperature, even below the glass-transition temperature, the free volume becomes zero at temperature T_0 , as shown in Figure 3. Then α_f is represented by

$$\alpha_f = \frac{f_g}{T_g - T_0} \quad (16)$$

If the relationship between the structure of a polymer and temperature T_0 is obtained, we can predict α_f . T_0 values of some polymers were obtained from measured values of f_g and α_f , as shown in Table II, and T_0 versus T_g was plotted in Figure 6. As shown in Figure 6, the plot shows two lines, one of which is made up of the polymers without side branch (solid line) and the other with side branch (dotted line), respectively. The solid line for polymers without side branch is represented by

$$T_0 = 0.88T_g \quad (17)$$

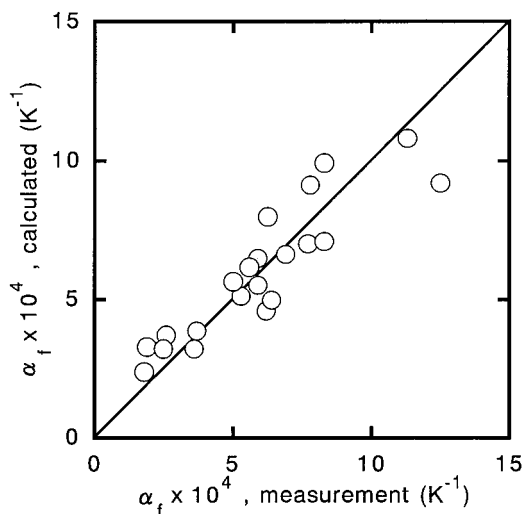


Figure 7 Comparison between the calculated and measured values of α_f . Calculated values are obtained by using eq. (19).

It seems that the deviation of T_0 of polymers with side branch from eq. (17) is greater with increasing size of the side branch. Therefore, we tried to establish a relationship by taking correction of the size of the side branch into consideration and obtained the following equations:

$$T_0 = 0.868T_g - 9.96 \frac{f_{SC}}{n_V} + 4.48 \quad (18)$$

and

$$\alpha_f = \frac{f_g}{0.132T_g + 9.96 \frac{f_{SC}}{n_V} - 4.48} \quad (19)$$

where f_{SC} is the number of statistical skeletal bonds in the side branch and n_V is the number of statistical skeletal bonds of the main chain in a repeat unit, respectively. The calculated and measured values of α_f are compared, as shown in Figure 7.

The reason for the correction of the side branch is not exactly known. Maybe it is related to the excess of free volume of side branch. It is well known that the glass-transition temperature is lowered with a decrease in its molecular weight.¹²⁻¹⁴ It is reasoned that this is because the end of the polymer chain has excess free volume, in that the polymer end is easier to move than its middle part. The number of molecular ends increases with the decrease in molecular weight, so excess of free volume is increased. For the same reason, the side branch can move more freely and has an excess of free volume.

Comparison between Predicted and Experimental Values

As described earlier, the quantitative structure-property relationship between zero-shear viscosity and molecular parameters of polymers is obtained from eq. (11). All molecular parameters included in this equation can be predicted by group contribution methods. To substitute these predicted values for eq. (11), zero-shear viscosity and its temperature dependence can be calculated.

The zero-shear viscosities of polystyrenes and polycarbonates with various molecular weights were calculated by using eq. (11). All molecular parameters were obtained by group contribution methods, as shown in Table III. The calculated zero-shear viscosities were compared with the measured ones in Figures 8 and 9. It appears that

Table III Calculated Molecular Parameters by Group Contribution Methods

	$\langle l_V^2 \rangle$ (Å)	m_V (g/mol)	C_∞	M_e (g/mol)	T_g (K)	f_g	$\alpha_f \times 10^4$ (K ⁻¹)
Polystyrene	2.34	52	10.7	20,000	369	0.032	6.4
Polycarbonate of bisphenol A	43.7	127	2.4	2150	418	0.043	7.1
Polysulfone	34.8	111	2.6	2260	472	0.035	5.9
Poly(ether sulfone)	34.7	116	2.8	2680	514	0.040	6.3
Phenoxy resin	12.4	47	3.7	1920	388	0.049	9.6
Polyethylene	2.34	14	6.1	1580	175	0.017	9.3
Polypropylene	2.34	21	9.1	11,000	254	0.019	5.6

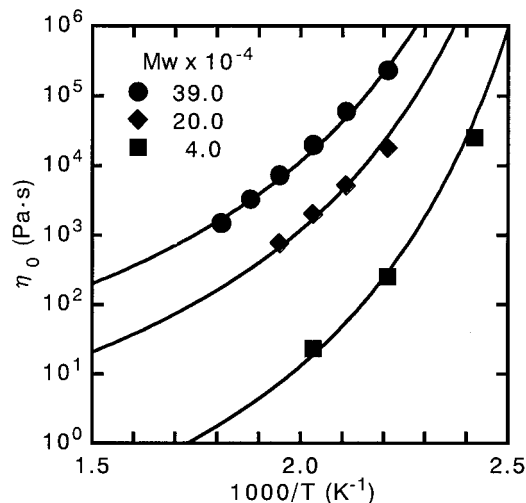


Figure 8 Comparison between the calculated and measured values of zero-shear viscosity of polystyrenes with various molecular weights. The solid lines are calculated values and the symbols are measured values. Calculated values are obtained by using eq. (11).

the measured values and the calculated values show quite good agreement.

For some other polymers, such as polysulfone, poly(ether sulfone), and phenoxy resin, both the measured and calculated values were compared, as shown in Figure 10, also showing quite good agreement.

It is generally believed that the temperature dependence of zero-shear viscosity is represented

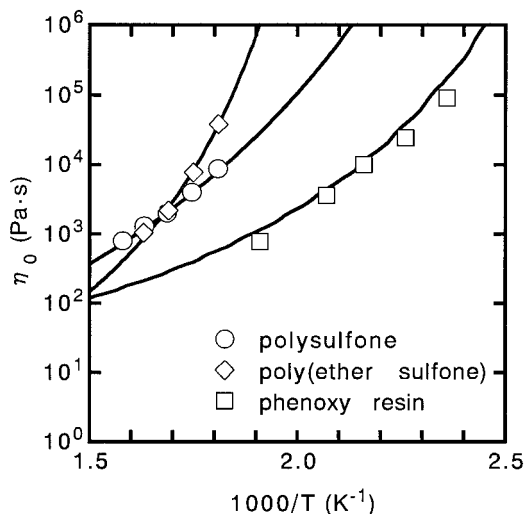


Figure 10 Comparison between the calculated and measured values of zero-shear viscosity of polysulfone, poly(ether sulfone), and phenoxy resin. The solid lines are calculated values and the symbols are measured values. Calculated values are obtained by using eq. (11).

by two different formulae, depending on the temperature range. For $T_g < T < T_g + 100$ K, temperature dependence obeys the WLF equation, which is applied to amorphous polymers; for $T > T_g + 100$ K, it obeys the Arrhenius equation, which is commonly applied to semicrystalline polymers. However, Lomellini^{15,16} reported that the WLF equation could be represented until about $T_g + 185$ K for polysty-

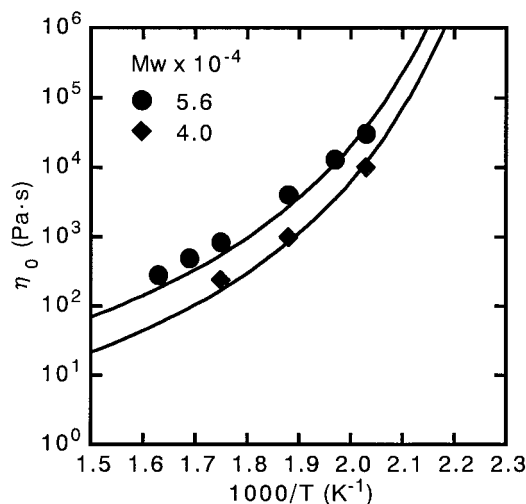


Figure 9 Comparison between the calculated and measured values of zero-shear viscosity of polycarbonates with various molecular weights. The solid lines are calculated values and the symbols are measured values. Calculated values are obtained by using eq. (11).

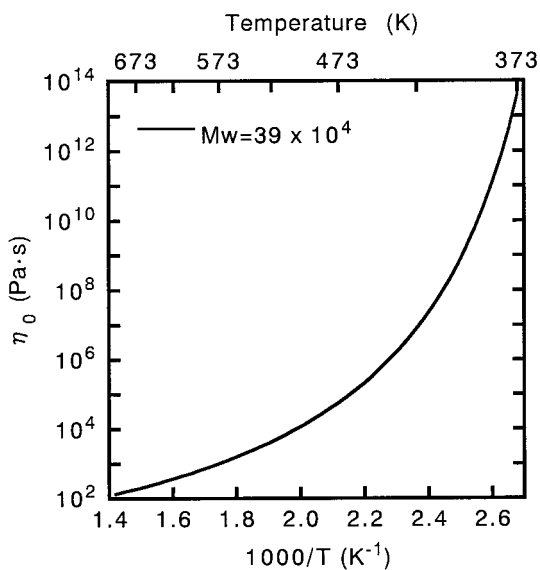


Figure 11 Typical WLF behavior of polystyrene with molecular weight $M_w = 39 \times 10^4$. The line is calculated by eq. (11).

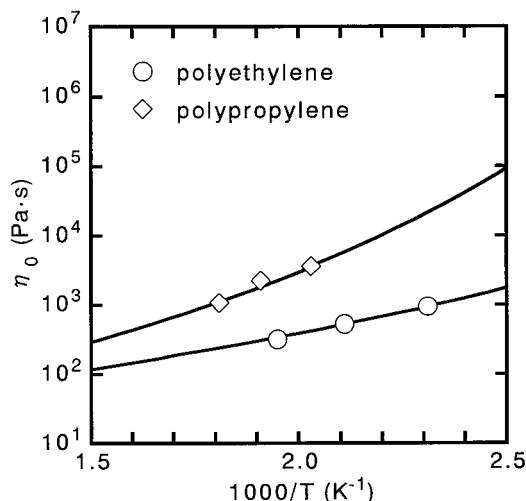


Figure 12 Comparison between the calculated and measured values of zero-shear viscosity of polyethylene and polypropylene. The solid lines are calculated values and the symbols are measured values. Calculated values are obtained by using eq. (11).

rene and polycarbonate and found no evidence of Arrhenius-like behavior in this region.

We maintain there is no difference between the WLF and Arrhenius-type behaviors. For example, the WLF behavior of polystyrene is plotted in zero-shear viscosity versus $1/T$ in Figure 11. The glass-transition temperature of polystyrene is 373 K. Observation of the temperature region between 373 and 473 K shows curvature; observation of the higher temperature region (e.g., 473–623 K) shows a straight line with a constant slope, like the Arrhenius-type behavior. We tried to predict the zero-shear viscosity of semicrystalline polymers, polyethylene, and polypropylene by eq. (11). All their molecular parameters are calculated by using group contribution methods described earlier. The calculated and measured values of zero-shear viscosity are presented in Figure 12, showing quite good agreement. On this figure the slopes of $\log \eta_0$ versus $1/T$ are almost constant.

As described before, this modified eq. (11) is very useful to calculate the zero-shear viscosity and its temperature dependence. By using group contribution methods, these values can be obtained from the molecular structure of polymers.

CONCLUSIONS

We propose a new relationship between molecular parameters and zero-shear viscosity of polymers,

such as mean square length and average molecular weight of statistical skeletal unit, characteristic ratio, entanglement molecular weight, glass-transition temperature, free volume fraction at glass-transition temperature, and thermal expansion coefficient of free volume. These molecular parameters can be predicted from the chemical structure of polymers by using group contribution methods. We propose use of the semiempirical equations relating free volume and structure of polymers, which are based on group contribution methods. The obtained values show quite good agreement with measured values.

APPENDIX

For a linear polymer, $g = 1$. Without solvent or diluent, $\varphi_2 = 1$ and usually $\nu_2 = 1$. So eq. (4) is rewritten

$$X = g \frac{\langle s^2 \rangle}{M} Z \frac{\varphi_2}{\nu_2} \quad (4)$$

$$X = \frac{\langle s^2 \rangle}{M} Z \quad (4')$$

From eqs. (4)', (8), (9), and (10)

$$X = \frac{C_\infty Z \langle l_V^2 \rangle}{6m_V}$$

$$X_C = \frac{C_\infty Z_C \langle l_V^2 \rangle}{6m_V} = \frac{C_\infty^3 \langle l_V^2 \rangle}{m_V}$$

So eq. (2) is rewritten

$$\eta_0 = F(X) \zeta(\rho) \quad (2)$$

$$\begin{aligned} \log \eta_0 &= \log F(X) + \log \zeta(\rho) \\ &= \log \left(\frac{N_A}{6} \right) + \log X_C + a \log \left(\frac{X}{X_C} \right) + \log \zeta(\rho) \\ &= \log \left(\frac{N_A}{6} \right) + \log \left(\frac{C_\infty^3 \langle l_V^2 \rangle}{m_V} \right) + 3.4 \log \left(\frac{M}{2M_e} \right) \\ &\quad + \log \zeta(\rho) \end{aligned} \quad (10)$$

and eq. (5) is

$$\zeta(\rho) = \zeta_{00} \exp\left(\frac{W}{T}\right) \exp\left[\frac{B}{f_g + \alpha_f(T - T_g)}\right] \quad (5)$$

where $\log \zeta_{00} = -10.6$, $\exp(W/T) = 1$, and $B = 1$ were assumed; then

$$\log \zeta(\rho) = -10.6 + \frac{1}{2.303} \left[\frac{1}{f_g + \alpha_f(T - T_g)} \right] \quad (11)$$

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