Melt Viscosity of Poly(diethylene glycol-co-succinic acid): Molar Mass Dependence in the Nonentangled Regime

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SYNOPSIS

Experimental and theoretical results are reported on the dependence of melt viscosity on the molar mass of poly(diethylene glycol-co-succinic acid) (DEG-SA) in the nonentangled regime. A power law described the behavior with an exponent of 2.09 ± 0.10 at 30°C and of 2.59 ± 0.09 at 90°C. The modified Rouse theory was used to describe the relationship between melt viscosity and molar mass. The parameters related to the modified Rouse theory were determined by the WLF equation and the free-volume theory. The WLF parameters of various samples were checked at their T_g, which is the reference temperature. Results confirmed that the free volume and the monomeric friction coefficient (ξ_0) dominate the behavior of the melt. The agreement between the calculated and experimental melt viscosity is satisfactory. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The dependence of the steady-flow shear viscosity (η) of polymer melts on the molar mass (M) is usually described by the power law[1,2]

$$\eta = KM^{\alpha} \tag{1}$$

where K is a constant and α is a power index. Here, the value of α is 3.5 ± 0.3 if the molar mass is greater than a characteristic value M_c, which is usually related to the average molar mass between entanglement points. At low molar masses, the value of η is directly proportional to M ($\alpha \approx 1$). The viscosity behavior can be described, e.g., by the Rouse theory.[3]

For polydispersed polymers, the weight-average molar mass, $\bar{M}_w$, is usually used to describe molar mass-dependent behavior in the entangled regime. There is a lively discussion in the literature concerning the influence of the width and modality of the molar mass distribution function on η (see Refs. 1 and 4–6). However, in the low molar mass region, the use of the number-average molar mass, $\bar{M}_n$, is

preferred because it can be directly related to the free volume.

For molar masses less than M_c, the entanglement coupling is no longer an important factor. The M dependence of the melt viscosity can be described by the Rouse model, which yields $\alpha \approx 1$ for the exponent in eq. (1). For the Rouse approximation, the range of molar masses in which the model is valid is limited at the upper end by M_c. At the lower end, this model is limited by the molar mass when the properties (such as the specific volume and the glass transition temperature, T_g) reach their limiting values.[1,7,8] For molar masses smaller than the lower limit, the value of α increases again with decreasing molar mass and becomes significantly greater than 1. The reason for this behavior is that the specific volume, T_g, and the average monomeric friction coefficient (ξ_0) decrease abruptly with decreasing molar mass. The dependence of the specific volume, T_g, and ξ_0 on M is attributed to the free volume associated with the number of macromolecular chain ends. In this article, we use the modified Rouse theory as it was derived by Ferry[1] to analyze the behavior of the melt viscosity of the saturated poly(diethylene glycol-co-succinic acid) with the molar mass. Experimental results and relationships obtained from the theory will be compared.

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The Modified Rouse Theory

The original Rouse theory[3] of linear viscoelastic properties applicable to dilute solutions of polymers is based on the coordination of different parts of a polymer chain. These parts are referred to as sub-molecules and represent portions of the polymer chain that are long enough to approximate a Gaussian probability distribution. The full expression of the viscosity of the dilute solution of the polymer in the Rouse model can be written in the following form:

$$\eta - \eta_0 = \frac{na^2 P^2 \xi_0}{36} = \frac{ca^2 N_A}{36 M_0^2} (\xi_0 M) \qquad (2)$$

where η and η_0 are the viscosities of dilute solution and solvent, respectively; n, the number of polymer molecules per unit volume ($n = cN_A/M$ for dilute solution); c, the concentration of the solution; N_A, Avogadro's constant; M_0, the molar mass of the repeat unit; and a, a parameter called the equivalent length. In eq. (2), a^2 represents the ratio of the mean-square end-to-end distance to the degree of polymerization (P) and ξ_0 accounts for the average frictional force per monomer unit experienced by a chain in the shear field. For a dilute solution, it is assumed that the monomeric friction coefficient is independent of the molar mass. Its magnitude, therefore, depends only on the viscosity of the solvent.

In accordance with the principle of Bueche,[9] the character of molecule motions and configurational changes is much the same in concentrated solution or even undiluted polymers as long as the molar mass is low enough that coupling entanglements do not occur. The only effect of changing the medium from solvent molecule to polymer molecule is an increase in the relaxation time. When applying the Rouse theory to undiluted, nonentangled polymer melts, the number of polymer molecules per unit volume is $\rho N_A/M$, rather than cN_A/M (where ρ is the density of the polymer). The term $\eta - \eta_0$ is replaced by η since there is no solvent. Therefore, the reformulated equation of the melt viscosity is given by the following formula[1,2]:

$$\eta = \frac{\rho a^2 N_A}{36 M_0^2} (\xi_0 M). \qquad (3)$$

In this equation, the dependence of ξ_0 on the molar mass is attributed to the free volume associated with the number of the chain ends. The corresponding

equation can be written in the following form:

$$\xi_0 = \xi_{00} \exp\left\{ B\left[\frac{1}{f_m} - \frac{1}{f_0} \right] \right\} \qquad (4)$$

where ξ_{00} represents the monomeric friction coefficient ξ_0 at high molar mass values where the molecular chain end effects can be neglected. In eq. (4), B is a constant close to unity and f_0 and f_m are the fractional free volumes at infinitely large molar mass and of an actual sample of the given polymer, respectively, at the same temperature. The fractional free volume increases with the number of chain ends in the same manner as does the specific volume.[10] Thus, the following relationship holds:

$$f_m = f_0 + A/\bar{M}_n \qquad (5)$$

where A is a constant related to the free volume per chain end. Thus, eq. (4) becomes

$$\xi_0 = \xi_{00} \exp\left\{ B\left[\frac{1}{f_0 + \dfrac{A}{\bar{M}_n}} - \frac{1}{f_0} \right] \right\}. \qquad (6)$$

In the free-volume theory,[1] the ratio a_T of a relaxation time at a given temperature T to the value it adopts at a reference temperature T^0 is represented by

$$a_T = \exp\left\{ B\left[\frac{1}{f} - \frac{1}{f^0} \right] \right\} \qquad (7)$$

where f and f^0 are the fractional free volumes at temperatures T and T^0, respectively. If f is assumed to increase linearly with temperatures between T and T^0 with a thermal expansion coefficient of the free volume, α_f, which can be given by the difference between the thermal expansion coefficient of the rubbery and the glassy state of the polymers, i.e., $f = f^0 + \alpha_f(T - T^0)$, then the following expression holds:

$$\log a_T = -\frac{(B/2.303 f^0)(T - T^0)}{(f^0/\alpha_f) + (T - T^0)}. \qquad (8)$$

In the usual derivation of the Williams–Landel–Ferry (WLF) equation, a_T is written in the following form[11]:

$$\log a_T = -\frac{C_1^0(T - T^0)}{C_2^0 + (T - T^0)} \qquad (9)$$

where $C_1^0 = B/(2.303f^0)$ and $C_2^0 = f^0/\alpha_f$. The molar mass dependence of the fractional free volume [eq. (5)] can be determined at a constant reference temperature T^0.

The temperature dependence of the melt viscosity is usually modeled with two different mechanisms acting in different temperature ranges:[6,11,12]

1. For $T > T_g + 100°C$, the free volume reaches a nearly constant value and the temperature dependence follows the Arrhenius equation:

$$\eta = K \exp\left(\frac{E_a}{RT}\right) \quad (10)$$

where K is a constant; R, the universal gas constant; and E_a, the activation energy of the flow, which is the energy related to a segment to jump from an occupied site to a hole.

2. For $T_g < T < T_g + 100°C$, the temperature effect is described by the WLF equation [see eq. (9)]. Here, the melt viscosity at temperature T is written by

$$\eta(T) = a_T \eta(T^0)\frac{T\rho}{T^0\rho^0} \quad (11)$$

where $\eta(T)$ and $\eta(T^0)$ are the melt viscosities at T and T^0, respectively, and ρ and ρ^0 are the densities at T and T^0, respectively. However, the ratio of $T\rho/T\rho^0$ is about unity and changes little over ordinary temperature ranges.[13] Thus, the WLF equation for the temperature dependence of the melt viscosity can be given by

$$\log a_T = \log \frac{\eta(T)}{\eta(T^0)}$$
$$= -\frac{C_1^0(T - T^0)}{C_2^0 + (T - T^0)} . \quad (12)$$

This equation is derived directly from the assumption that the free volume is a linearly increasing function of temperature from T_g to $T_g + 100°C$. Furthermore, the apparent activation energy can be defined as

$$E_a = R \frac{d\ln(a_T)}{d(1/T)} . \quad (13)$$

For the WLF behavior, E_a is given by

$$E_a = \frac{2.303 R C_1^g C_2^g T^2}{[C_2^g + (T - T_g)]^2} \quad (14)$$

where C_1^g and C_2^g are the WLF parameters at T_g as a reference temperature.

Our approach will be to use the temperature dependence of η or the WLF equation to obtain f_m, to use eq. (5) to obtain the values of the two constants f_0 and A, and to use the principle according to which ξ_0 will reach its limiting value at sufficiently high $\bar{M}_n$ to obtain the value of ξ_{00}.[2,14] With these parameters, the melt viscosity of the polymer can be predicted theoretically. The full expression for $\eta(\bar{M}_n)$, which is the modified Rouse model used in our study, is given by

$$\eta = \frac{\rho a^2 N_A}{36 M_0^2} \bar{M}_n \xi_{00}$$
$$\times \exp\left\{B\left[\frac{1}{f_0 + \dfrac{A}{\bar{M}_n}} - \frac{1}{f_0}\right]\right\} . \quad (15)$$

O'Connor and Scholsky[7] used a similar theoretical description to calculate the melt viscosity of various low molar mass poly(methyl methacrylate) (PMMA) samples. The C_1^0 constant was obtained in O'Connor and Scholsky's study from the WLF equation, and f_0 and A were obtained by using a linear least-squares fit to eq. (5). The other constants were taken from the literature.[1] An acceptable agreement was obtained between experimental and calculated viscosities for PMMA.

EXPERIMENTAL

A synthesis of saturated polyesters of diethylene glycol (DEG) and succinic acid (SA) was obtained by melt polycondensation at 180°C using a molar ratio of DEG/SA of 1.02 (see, e.g., Ref. 15). Samples with low molar masses were easily prepared, and specimens with higher molar mass (greater than 2000 g mol^{-1}) polyesters were obtained by adding a catalyst (0.4 mol % of SnCl$_2$) to the oligomer during the polycondensation. The reaction mixture was evacuated during the polycondensation at high conversion to remove the condensation product H$_2$O.

The value of $\bar{M}_n$ was determined by end-group titration and ebulliometry. Titration of terminal COOH was performed in tetrahydrofuran using

NaOH and bromothymol blue as the indicator. If the principle of equal reactivity during the condensation reaction is fulfilled, then the probability of having carboxylic or alcoholic chain ends is equal and COOH titration results in $\bar{M}_n$ values. This was a valid approximation, as we confirmed in a previous study.[15] For the samples with the three highest molar masses, the $\bar{M}_n$ values were obtained by ebulliometry using a device built in the laboratory of Prof. J. E. Guillet. The construction of this instrument was similar to that described by Ray.[16] The value of the instrumental constant was determined by using tristearin ($\bar{M}_n$ = 891.5 g mol^{-1}) dissolved in toluene. The ebulliometry experiment consists of successively adding 4–5 portions of polyester samples, usually totaling 120 mg, to the preconditioned ebulliometer, and recording the boiling point elevation of each portion.

The T_g of various samples were measured by using a Perkin-Elmer DSC 7 instrument. T_g was taken as the temperature corresponding to the midpoint of the change in the heat capacity from the onset to the endset of the glass transition (or from the glassy to the rubbery state). The sample size was 10–15 mg and a heating rate of 10°C/min was utilized. The temperature scale of the instrument was calibrated by using a two-point calibration with decane and indium samples.

Steady shear melt viscosity of various polyester samples was measured with a Brookfield programmable rheometer Model DV-III equipped with a Thermosel system and Small Sample Adapter accessories. The shear rates were measured at a number of different temperatures for each sample. No shear-rate dependence was observed for data presented in this paper, i.e., η values obtained correspond to nonshear or zero-shear viscosities, and the data represent a Newtonian behavior. The calibration of the rheometer was verified by comparing the quoted viscosity values of a standard silicon oil (HT30,000, Brookfield Eng. Labs. Inc.) at three temperatures with measured values. In all cases, agreement was better than ±2%.

The density was measured by a calibrated pycnometer at both 30 and 90°C, respectively, using light mineral oil. The densities for samples with 440, 1062, and 4295 g mol^{-1} molar mass were measured, whereas the other values were estimated from the following equation[10]:

$$1/\rho = a + b/\bar{M}_n \qquad (16)$$

where a and b are constants. The density values of the samples are shown in Table I.

Table I   The Density of Poly(DEG-SA) Samples

PES(DEG-SA) $\bar{M}_n$ (g mol^{-1})	Density ρ (g cm^{-3})	
	30°C	90°C
440[a]	1.2515	1.2000
681	1.2561	1.2036
761	1.2566	1.2041
985	1.2577	1.2055
1062[a]	1.2622	1.2086
1145	1.2629	1.2084
2674	1.2663	1.2157
4295[a]	1.2738	1.2251
7144	1.2889	1.2427

[a] Experimental data; other values were estimated [see eq. (16)].

RESULTS AND DISCUSSION

The number-average molar mass of the polyester samples, required for the calculation of η, was obtained by COOH end-group titration for $\bar{M}_n \leq 1145$ g mol^{-1} and by ebulliometry for $\bar{M}_n > 1145$ g mol^{-1}. Ebulliometry was chosen to measure $\bar{M}_n$ of samples with higher molar masses due to its better accuracy in this M range compared with the end-group titration technique. The values of $\bar{M}_n$ of polyester samples are shown in Table II together with the glass transition temperatures obtained by DSC. As previously discussed,[15,17] the T_g behavior on the molar mass for polyester samples with low degree of polymerization can be described by the Fox–Flory relationship that is based on the free-volume theory[10]:

$$T_g = T_{g,\infty} - k/\bar{M}_n \qquad (17)$$

where $T_{g,\infty}$ is the glass transition temperature in the limit of infinite molar mass, and k, a constant that is proportional to the excess free volume per chain end. The fit of our data by eq. (17) is excellent with values of $T_{g,\infty}$ = −29.03 ± 0.06°C, k = 9.07 ± 0.05 × 10^3 g °C mol^{-1}, and a regression coefficient, r = .9999.

Figure 1 shows the melt viscosities of polyester samples at two different temperatures as a function of the number-average molar mass $\bar{M}_n$. The melt viscosities of samples cannot be described by the Rouse prediction, i.e., the melt viscosity is not directly proportional to $\bar{M}_n$. The melt viscosity vs. $\bar{M}_n$ curves have an average slope of 2.09 ± 0.10 to 2.59 ± 0.09 at 30 and 90°C, respectively. It is clear that the sensitivity of η to $\bar{M}_n$ is related to the free-volume

Table II $\bar{M}_n$ **and** T_g **of Various PES(DEG-SA)**

| PES(DEG-SA) Acid No.[a]	T_g (°C)	$\bar{M}_n$ (g mol^{-1})	
		Titration	Ebulliometry
128	−49.6	440	
82	−42.5	681	
74	−40.9	761	
57	−38.2	985	
53	−37.6	1062	
49	−37.0	1145	
21	−32.4		2622
13	−31.3		4295
8	−30.2		7144

[a] The acid no. (mg KOH/g PES in end-group titration) of each sample is used to identify the samples.

effects mentioned earlier. Thus, to describe the melt viscosity of these samples, the Rouse approach must be modified. In the following section, we describe our attempt to fit the data shown in Figure 1 by using the WLF equation and the free-volume approach. First, we will discuss the temperature dependence of η.

The melt viscosity of various samples at different temperatures was measured and the results are shown in Figure 2, where the lines were fitted by the WLF model [eq. (12)]. From the WLF fits, the parameters C_1^0 and C_2^0 can be obtained by linear regres-
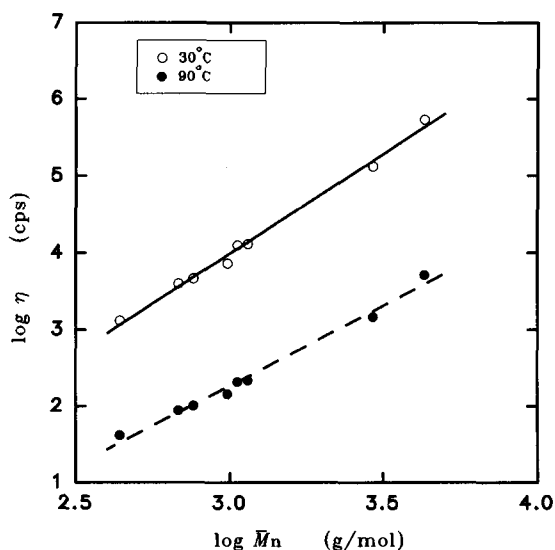
Figure 1 Log–log plot of zero-shear viscosity η as a function of the number–average molar mass at 30 and 90°C. The solid and the dashed lines are fitted by the power law with power indices of 2.09 at 30°C and 2.59 at 90°C, respectively.
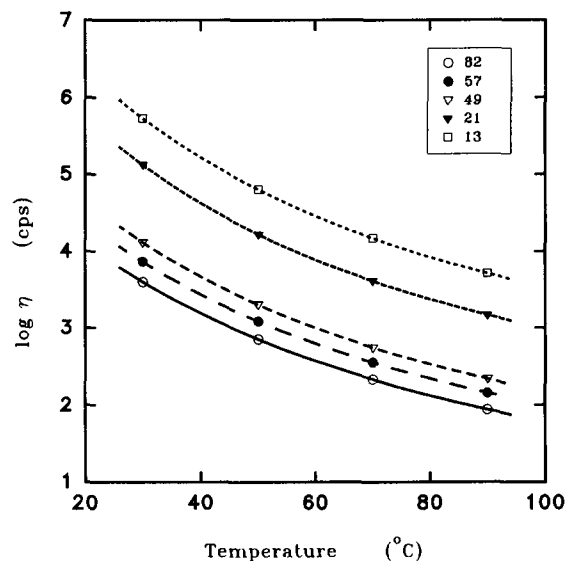
Figure 2 Log η vs. temperature for several polyester samples. The lines are fitted by the WLF model. The molar mass of samples increases from the bottom to the top in the graph. The different symbols used correspond to different acid numbers shown in the insert.

sion plotting $(T - T^0)/\log a_T$ against $T - T^0$. The values of C_1^0 and C_2^0 that we obtained are shown in Table III. As pointed out by Prest and Porter,[18] the WLF parameters are rather sensitive to experimental errors. However, the reliability of the results can be tested by checking each C_1 and C_2 at T_g, which is the reference temperature. The basis of this consistency test, as it was concluded by Williams, Landel, and Ferry,[1,11] is that C_1^g and C_2^g can be considered "universal constants" after calculating the average values of C_1^g and C_2^g by fitting data on a large number of polymers. The following equations are used to calculate the values of C_1^g and C_2^g.

$$C_2^g = C_2^0 - T^0 + T_g \tag{18}$$

$$C_1^g = \frac{C_1^0 C_2^0}{C_2^0 - T^0 + T_g} . \tag{19}$$

The values of C_1^g and C_2^g of our polyesters were tabulated in Table III. It can be seen that they are quite consistent within the temperature range (30–90°C) and the average values of C_1^g and C_2^g are independent of the temperature and the molar mass, with the exception of the lowest molar mass sample. Moreover, the average values of the apparent activation energy calculated according to eq. (14) decreased with increasing temperature from 30 to 90°C (see Table III).

Table III WLF Parameters and Apparent Activation Energies at 30 and 90°C

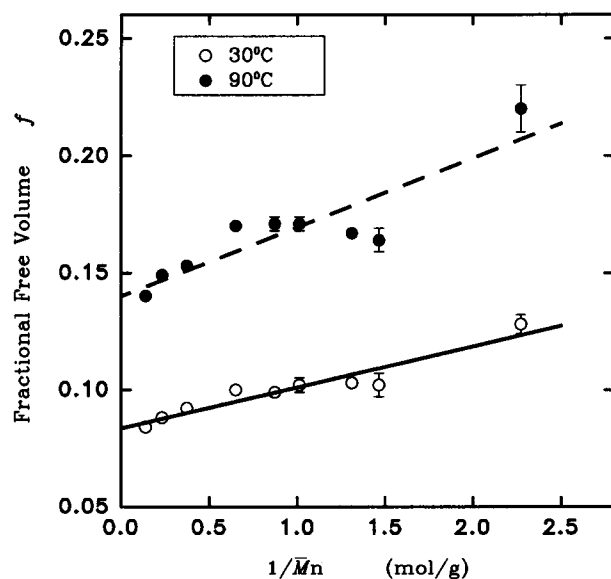| Acid No.	30°C					90°C				
	C_1^0	C_2^0	C_1^g	C_2^g	f_g/B	C_1^0	C_2^0	C_1^g	C_2^g	f_g/B
128	3.56 ± 0.13	81.68 ± 3.60	140.1	2.08	0.003	2.29 ± 0.12	150.9 ± 7.9	30.36	11.42	0.014
82	4.24 ± 0.04	93.56 ± 1.01	18.88	21.05	0.023	2.65 ± 0.04	156.2 ± 2.6	17.37	23.80	0.025
74	4.22 ± 0.02	92.32 ± 0.44	17.37	22.76	0.025	2.61 ± 0.03	153.9 ± 1.7	17.37	23.18	0.025
57	4.24 ± 0.01	89.19 ± 0.09	18.09	20.99	0.024	2.55 ± 0.01	149.5 ± 0.4	18.09	21.32	0.024
53	4.43 ± 0.01	93.93 ± 0.01	18.09	22.07	0.024	2.65 ± 0.03	149.5 ± 1.7	18.09	21.87	0.024
49	4.40 ± 0.05	88.34 ± 1.18	18.09	21.37	0.024	2.54 ± 0.05	145.4 ± 2.7	19.74	18.50	0.022
21	4.72 ± 0.04	85.06 ± 0.78	18.09	22.66	0.024	2.84 ± 0.04	147.3 ± 2.2	17.37	21.40	0.025
13	4.93 ± 0.01	86.41 ± 0.14	16.70	25.12	0.026	2.92 ± 0.01	146.9 ± 0.5	16.70	24.87	0.026
8	5.00 ± 0.10	83.50 ± 1.92	16.08	27.71	0.027	3.10 ± 0.96	148.8 ± 1.0	16.70	25.78	0.026
Average values[a]			17.64 ± 0.73	22.74 ± 1.62	0.025 ± 0.002			17.50 ± 0.68	23.25 ± 1.84	0.025 ± 0.002
Average activation energy[a] (kJ/mol)			86.40					45.60		

C_1^0 and C_2^0 refer to the reference temperature T^0. C_1^g and C_2^g are calculated from the corresponding C_1^0 and C_2^0 using eqs. (18) and (19), and f_g/B is calculated by the use of Eq. (20).
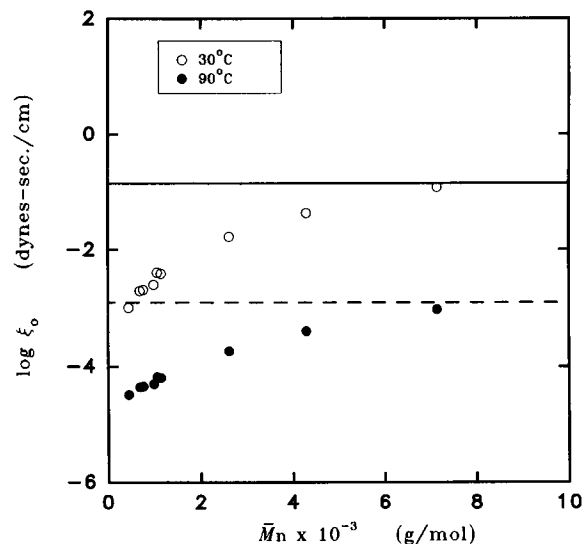[a] The average values were calculated without the sample of acid number 128.

As mentioned earlier, the fractional free volume f can be obtained from the WLF parameters according to the relationship $f = B/(2.303C_1^0)$, where B is taken to be unity. The values of f_0 and A were obtained from the molar mass dependence of f by using eq. (5). Figure 3 shows a plot of f vs. $1/\bar{M}_n$ at 30 and 90°C. A linear least-squares fit of these data yields $f_0 = 0.0803 \pm 0.0024$, $A = 30.51 \pm 0.01$ g mol^{-1} at 30°C, and $f_0 = 0.1330 \pm 0.0017$, $A = 56.49 \pm 0.05$ g mol^{-1} at 90°C.

Figure 4 is the plot of log ξ_0 vs. $\bar{M}_n$. The ξ_0 values were calculated from eq. (3), where $a = 7.0 \pm 0.05 \times 10^{-8}$ cm and $M_0 = 188.17$ g mol^{-1}. The parameter a was chosen by comparing the glass transition temperature and the molar mass of our polyester with other polymers having known a values.[1] As we can see, the monomeric friction coefficient increased and gradually reached a limiting value at a sufficiently high molar mass. For poly(DEG-SA), the limiting values of the logarithmic monomeric friction coefficient were estimated to be log $\xi_{00} = -0.85$ at 30°C and log $\xi_{00} = -2.90$ at 90°C (units are dynes-s cm^{-1}).

Figure 5 shows the experimental log η vs. the log $\bar{M}_n$ relationship with the calculated curves obtained from eq. (15). The good agreement between calculated and experimental curves demonstrates that eq. (15) describes the melt viscosity–molar mass relationship reasonably well in the low molar mass regime. The parameters required to perform the calculations of the modified Rouse approximation were

Figure 4 Plot of log ξ_0 vs. $\bar{M}_n$ at 30 and at 90°C. The solid and dashed lines represent the limiting values of the monomeric friction coefficient.

either measured or calculated as described earlier. Assuming that only a few parameters ($\xi_0, f_0,$ and A) were fitted and that there is no adjustable parameter in the melt viscosity fit, the agreement is good. At 90°C, the experimental melt viscosities are slightly lower than the calculated results, whereas at 30°C, the agreement is within the experimental error.

Equation (15) contains several parameters such as $\xi_{00}, f_0, A, B,$ and a^2. The precise determination of these parameters is the key factor to achieve an
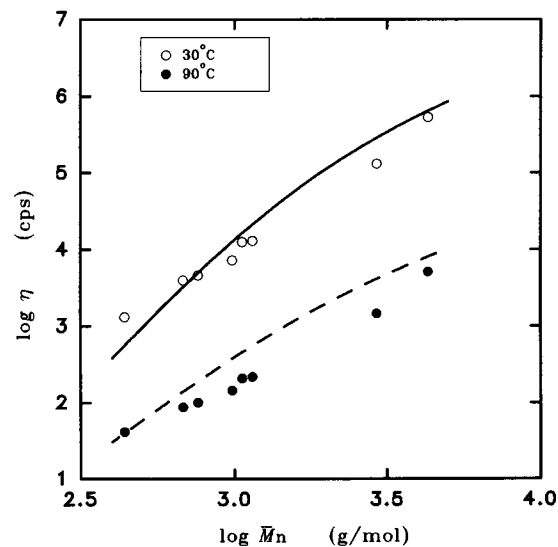

Figure 3 Plot of the fractional free volume vs. $1/\bar{M}_n$ at 30 and at 90°C. The solid and dashed lines are the linear least-square fits from which the constants A and f_0 were obtained.

Figure 5 Log–log plot of zero-shear viscosity η as a function of the number-average molar mass at 30 and at 90°C. The solid and the dashed lines are the calculated results by the modified Rouse model.

even better agreement between experimental and calculated results. Therefore, the values of all the parameters and their influence on the form of the $\eta(\bar{M}_n)$ relationship require further examination. First of all, the constant B has been taken as unity throughout our calculations. If this is not assumed, then the WLF parameter C_1 yields f/B rather than f. It is also of interest to examine the fractional free volume of the samples at their glass transition temperatures. This is accomplished by the following equation[1]:

$$f_g/B = (C_2^0 + T_g - T^0)/2.303C_1^0C_2^0. \quad (20)$$

The values of f_g/B are shown in Table III. With some scattering of data, the average values are approximately 0.025 ± 0.002 and show no trend with the molar mass and the reference temperature. This average value of f_g/B is in excellent agreement with data reported in literature[1,11] for many polymers.

The experimental melt viscosities at 90°C are lower than the calculated results (see Fig. 5). The main reason might be due to the high temperature, which is higher than $T_g + 100°C$ in this case. However, Lomellini[19] indicated that the limit of applicability of the WLF equation can be expanded to $T_g + 185°C$ for polystyrene and polycarbonate by a study of the dynamic melt viscosity. This conclusion seems to justify the use of the WLF model in our calculations.

A possibility to improve the agreement between experiment and theory is to study the effect of the parameter B at 90°C on the $\eta \sim \bar{M}_n$ relationship. In eq. (15), B is the only parameter that lacks clear physical interpretation. We used a value of $B = 1$, which is usually applied. In the literature,[1,2] values of B reported are in the range of 0.9 ± 0.3. It seems that if we include an adjustable parameter in our calculation, the best parameter to be varied would be B. If we review eq. (5) again, because the WLF parameter C_1^0 yields f/B rather than f, parameter A obtained by the linear least-squares fit should be corrected to be A/B. The value of f_0/B of our polyesters at 90°C is 0.1330 ± 0.0017, and the ratio is independent of the value of B. Figure 6 shows the response of the melt viscosity by changing the value of B from 1.0 to 0.6. The curves of η vs. $\bar{M}_n$ were depressed by more than one order of magnitude, and it seems that a B value of ca. 0.7 would give the best result.

Berry and Fox[2] indicated that it is convenient to take the melt viscosity at a molar mass slightly below the characteristic value M_c for the onset of entan-
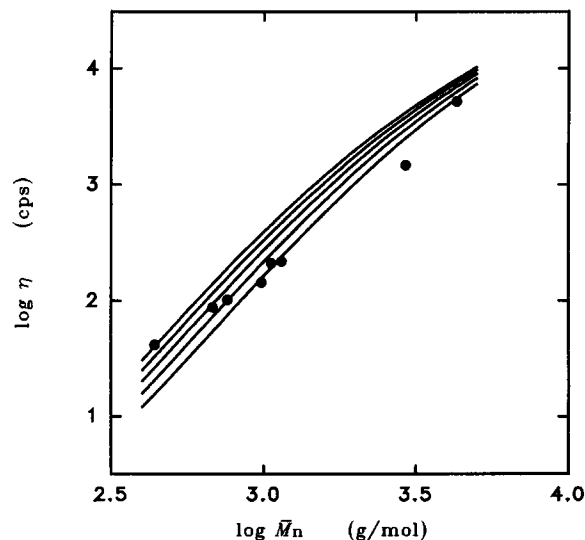
Figure 6 Log η vs. log $\bar{M}_n$ at 90°C. The lines represent the influence of the variation of B. From the upper to lower line, the corresponding values of B are 1.0, 0.9, 0.8, 0.7, and 0.6.

glement coupling. This is done in order to obtain the limiting monomeric friction coefficient ξ_{00} for molar masses that are sufficiently high to avoid the effects of the chain ends. In this region, it can be assumed that ξ_0 has already reached its limiting value of ξ_{00}. They also found that the value of ξ_{00} determined experimentally from eq. (3) agrees approximately with that derived independently from viscoelastic measurements, i.e., from the relaxation spectrum in the transition zone, for several polymers. Thus, the values of ξ_{00} in our calculation, obtained from the sample with the highest molar mass of poly(DEG-SA), were reliable.

The deviation of our calculated curve in Figure 5 from the experimental data at the lowest molar mass at 30°C could be due to the limited applicability of the modified Rouse theory[13] to samples with low molar mass utilized in this study. The theory is based on a bead-spring model without hydrodynamic interaction among beads. To use this theory effectively, the end-to-end distance of submolecules within macromolecules must be Gaussian. Therefore, the validity of the submolecule concept and the assumed Gaussian submolecule statistics might be questioned for our polyester samples at the lowest molar mass.

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