

## Viscoelastic Properties of Narrow-Distribution Polymers. II. Tensile Creep Studies of Polystyrene

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**ABSTRACT:** Tensile creep measurements were made on seven narrow-distribution polystyrene samples. The range of molecular weights was from  $7.50 \times 10^4$  to  $2.90 \times 10^6$  and that of temperature from 96 to 198°C. The data were all reduced to 140°C by the method of reduced variables. The shift factors were identical for all samples and followed the WLF equation. The free volume parameters were calculated by the method of Williams; the fractional free volume at  $T_g$  was 0.028 and the constant  $B$  in the Doolittle equation was 0.97. In the transition zone, all master curves, except that of the highest molecular-weight sample L-1, coincided. The master curve of sample L-1, shifted to the right on the logarithmic time scale by a factor of about 0.6, compared with those of other samples, and the retardation spectrum  $L(\tau)$  disappeared in the rubbery zone. A close relationship between these two observations was suggested. The average molecular weight between entanglements was independent of molecular weight as evaluated by ordinary methods. The dependences on molecular weight of the quantities,  $\eta_l$ ,  $D_e$  and  $\tau_m$ , were also examined. It was found that  $\eta_l$  and  $\tau_m$  varied as 3.3 power of molecular weight and  $D_e$  was independent of molecular weight.

**KEY WORDS** Viscoelasticity/Narrow-Distribution Polymers/Tensile Creep / Polystyrene / Steady-State Compliance / Tensile Viscosity / Relaxation Time / Molecular Weight / Entanglement / Retardation Spectrum /

In an earlier paper,<sup>1</sup> we have studied the viscoelastic properties of seven narrow-distribution poly( $\alpha$ -methylstyrene) samples by tensile creep measurements, and shown that the creep behavior in the terminal zone is quite different from that predicted by the Rouse—Buech theory (RB theory)<sup>2,3</sup> and also by the Ferry—Landel—Williams theory (FLW theory).<sup>4</sup> That is, the steady-state compliance is almost independent of molecular weight in the region of high molecular weights. A similar discrepancy has been also reported by other workers.<sup>5,6</sup> Furthermore the tensile viscosity shows a negative deviation from the familiar 3.4 power law in the range of molecular weights higher than  $2.0 \times 10^4$ . Such serious discrepancies between the existing theories and experimental results indicate the necessity of performing further experimental studies on other narrow-distribution polymers.

We here present results of tensile creep measurements performed on seven narrow-distribution polystyrenes of molecular weights from

$7.5 \times 10^4$  to  $2.9 \times 10^6$ .

### EXPERIMENTAL

#### Materials

Polystyrenes prepared by the anionic polymerization technique were generously provided by Prof. S. Onogi and Dr. T. Masuda of Kyoto University. Tails of the molecular weight distribution in the lowest and highest ends were eliminated by a fractionation at 35°C using a large-scale elution column with benzene—ethyl alcohol mixtures. The number-average molecular weight,  $M_n$ , was determined by osmometry in toluene at 37°C using a high-speed membrane osmometer (Mechrolab Model 502). The viscosity—average molecular weight,  $M_v$ , was calculated from intrinsic viscosity using the expression,<sup>7</sup>  $[\eta]_\theta = 8.0 \times 10^{-4} M_w^{0.50}$  (cyclohexane, 35°C). The weight-average molecular weight,  $M_w$ , was determined from the sedimentation equilibrium method. The number-average, vis-

cosity—average and weight-average molecular weights of samples are given in Table I, which indicates that their molecular weight distributions are very sharp.

Table I. Monodisperse polystyrene

Sample	$M_n$	$M_v$	$M_w$
L-1 <sup>a</sup>	—	$2.90 \times 10^6$	$2.60 \times 10^6$
L-2 <sup>a</sup>	—	$1.04 \times 10^6$	$1.06 \times 10^6$
L-40	$6.30 \times 10^5$	$6.50 \times 10^5$	—
L-41	$2.52 \times 10^5$	$2.75 \times 10^5$	—
L-39	$1.65 \times 10^5$	$1.90 \times 10^5$	—
L-38	$1.22 \times 10^5$	$1.22 \times 10^4$	—
L-36	$7.80 \times 10^4$	$7.50 \times 10^4$	—

<sup>a</sup>  $M_w/M_n$  is estimated to less than 1.05 from the sedimentation velocity boundary curve.

For tensile creep measurements, thin films were obtained by slow evaporation of solvent from 1–5% methylene chloride solutions on a clean mercury surface. To remove final traces of the solvent the films were completely dried in a vacuum oven for more than 10 days, annealed at 130° for 2 hr. and stored *in vacuo* at room temperature. The sample film dimensions ranged from 1.5 to 5.0 cm in length, from 0.5 to 1 cm in width and from  $2 \times 10^{-2}$  to  $4 \times 10^{-2}$  cm in thickness.

#### Method

The tensile creep measurements were made with a creep balance type apparatus which was described in detail previously.<sup>1</sup> The temperature was regulated within  $\pm 0.2^\circ\text{C}$  in the whole temperature range from 96 to 198°C. Argon (the purest grade) was passed through the creep apparatus at above 170°C as a precaution against thermal degradation. The maximum tensile strain including viscous flow did not exceed 16%. The variations of the cross-sectional area of films with elongation were corrected based on the assumption of volume constancy.

The densities and volume—temperature coefficients of samples were determined by dilatometry.

## RESULTS

The tensile creep compliance  $D(t)$  of sample L-41 is plotted logarithmically against time  $t$  in

Figure 1 at 12 different temperatures from 97.3 to 157.7°C. The glass transition temperature was 94.0°C as determined by dilatometry. Measurements commenced at 97.3°C after a period of thermostating, about 5 hr, which ensured that the sample had reached equilibrium

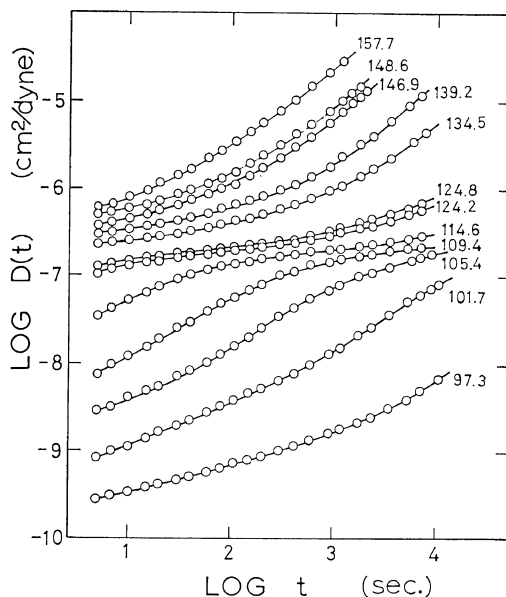


Figure 1. Tensile creep compliance of sample L-41, plotted logarithmically against time at the 12 temperatures indicated.

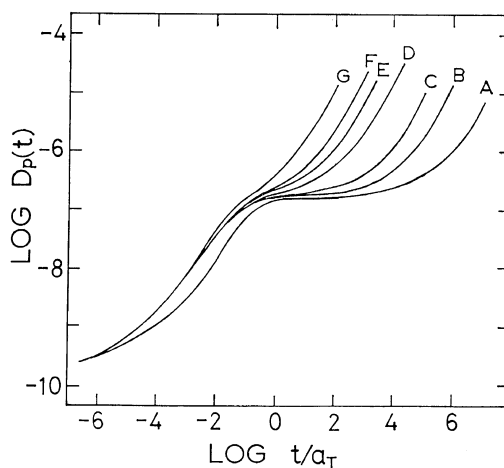


Figure 2. Tensile creep compliance of seven polystyrene samples reduced to 140°C: (A) L-1; (B) L-2; (C) L-49; (D) L-41; (E) L-39; (F) L-38; (G) L-36.

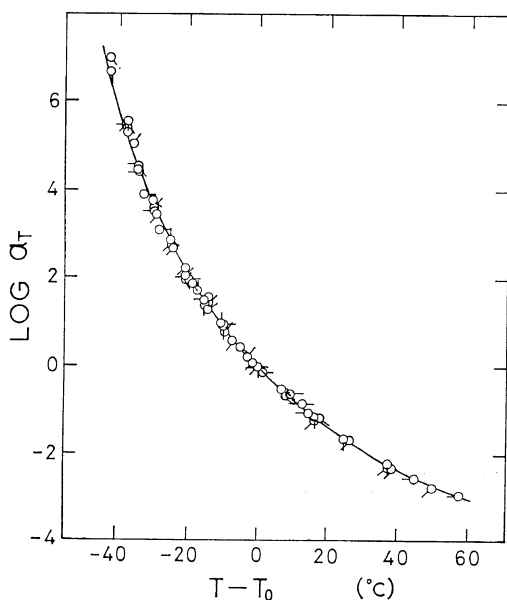
volume. At every other temperature special care was taken to take measurements in the voluminal equilibrium of samples. Families of creep curves similar to those given in Figure 1 were obtained for other samples.

The results for each sample were reduced to 140°C by the method of reduced variables to give the master curves illustrated in Figure 2. Here the subscript  $p$  denotes that the tensile creep compliance has been multiplied by a factor  $T\rho/T_0\rho_0$ , where  $\rho$  and  $\rho_0$  are the densities at the temperature of measurement  $T$  and the reference temperature  $T_0$  chosen as 140°C for all samples. The density  $\rho$  was calculated from eq 1 derived from the dilatometric measurements

$$\frac{1}{\rho} = 0.973 + 5.80 \times 10^{-4} (T - 94.0), \quad (1)$$

$T > 94.0^\circ\text{C}$

where 0.973 is the equilibrium specific volume at the glass transition temperature. For the purposes of clarity, the original data are not shown. However they lie within 5% of the master curves for all samples.



**Figure 3.** Log  $a_T$  against  $T - T_0$  for seven polystyrene samples. Sample key: pip up, L-36. successive 45° rotation clockwise, L-38, L-39, L-41 L-49, L-2, and L-1.

In Figure 3 the shift factor,  $a_T$ , used for the reduction is plotted semi-logarithmically against  $T - T_0$ . As can be readily seen in Figure 3, the shift factors for all samples coincide in the whole temperature region studied and follow the WLF equation<sup>8</sup>

$$\log a_T = -\frac{7.55(T - T_0)}{92.0 + T - T_0} \quad (2)$$

in which the numerical constants are determined by plotting  $-(T - T_0)/\log a_T$  against  $T - T_0$ .

## DISCUSSION

### Temperature Dependence

The shift factor  $a_T$  is generally expressed in terms of the relative free volume  $f$ , *i.e.*,

$$\log a_T = \frac{B}{2.303} \left( \frac{1}{f} - \frac{1}{f_g} \right) \quad (3)$$

$$f = \frac{v - v_0}{v_0} = f_g + \alpha_f(T - T_g) \quad (4)$$

where  $B$ , from the Doolittle equation  $\eta = A \exp(B/f)$ ,<sup>9</sup> is constant of the order of unity;  $f$  and  $f_g$  are the relative free volumes at  $T$  and  $T_g$ , respectively;  $v$  and  $v_0$  are the total and occupied specific volumes and  $\alpha_f$  is the thermal expansion coefficient of  $f$ . Combining eq 3 with eq 2, free volume parameters can be calculated. However, in eq 3, there are three free volume parameters,  $B$ ,  $f_g$ , and  $\alpha_f$  to be determined, while in eq 2 there are only two numerical constants. Thus, Williams, Landel, and Ferry have identified  $B$  rather arbitrarily to unity and evaluated  $f_g$  and  $\alpha_f$ . The application of this WLF analysis to the present data leads to  $f_g = 0.029$  and  $\alpha_f = 6.25 \times 10^{-4}$ . These values are somewhat higher than the universal values,  $f_g = 0.025$  and  $\alpha_f = 4.8 \times 10^{-4}$  offered by them. Moreover, the fact that  $\alpha_f$  is larger than the thermal expansion coefficient of the liquid given in eq 1 clearly indicates the failure of the WLF analysis.

Thus we again calculated the free volume parameters by the alternative procedure proposed by Williams.<sup>10</sup> Assuming that  $\alpha_f$  is equal to  $1/v_0 \cdot (dv/dT)_l$  where  $v_0$  is the constant occupied volume independent of temperature and  $(dv/dT)_l$  is the volume-temperature coefficient of the liquid, we can rewrite eq 3 as

$$\log a_T = - \frac{[v_0 B / 2.303 (v_g - v_0)] (T - T_g)}{(v_g - v_0) / (dv/dT)_l + (T - T_g)} \quad (5)$$

Since  $v_g$  and  $(dv/dT)_l$  are directly measurable macroscopic quantities, the parameters  $B$  and  $f_g$  (or  $v_0$ ) can be determined from eq 5.  $B$  and  $f_g$  thus determined are 0.97 and 0.028, respectively, which are in reasonable agreement with Williams values<sup>10</sup> of  $B = 0.91$  and  $f_g = 0.029$  derived from the polystyrene viscosity data and also with  $B = 0.85$  and  $f_g = 0.028$  obtained for viscous flow from polystyrene creep recovery data by Plazek.<sup>11</sup>

#### Transition Zone

In Figure 2, all the master curves except that of the highest molecular-weight sample, L-1, coincide in the transition zone, but the curve of L-1 shifts to the right on the logarithmic time scale by a factor of 0.6. When we compare the original creep curve of L-1 with those of other samples at the same temperature, the aspect of the shift becomes clearer. In Figure 4, the logarithmic plots of  $D(t)$  vs.,  $t$  at 102.1°C

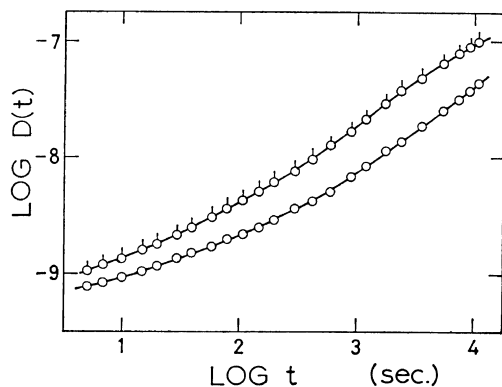


Figure 4. Tensile creep compliance of L-1 is compared with that of L-2 at 102.1°C. No pip, L-1; pip up, L-2.

are given for L-1 and L-2. The shift is a rather startling phenomenon, because the shift factor of L-1 coincided with those of other samples in the whole temperature region.

According to the current molecular theory,<sup>12</sup> the position of the transition zone on the time scale is related to the monomeric friction constant  $\zeta_0$ . In the case of a homologous series of

low molecular-weight polymers, a shift of the transition zone was also observed as the molecular weight was varied and it can be quantitatively interpreted in terms of the molecular weight dependence of  $\zeta_0$  or, in other words, the effect of chain end on the free volume. In the range of molecular weights studied here, however, the glass transition temperature is almost independent of molecular weight. This was confirmed by torsion pendulum measurements, though an uncertainty of 1–2°C was involved in the estimation of  $T_g$ . Even if the value of  $T_g$  of the L-1 sample were 2°C higher than that of the L-2, it would cause a displacement of the master curve of the former to right only by a factor of about 0.16, which is much smaller than the observed shift. Thus it is difficult to give an adequate explanation of the observed facts in terms of the variation of free volume with molecular weight. Furthermore, the shift can be ascribed to neither branching of the sample nor residual stress (or strain) in the film, because the anionic polymerization technique gives a linear polymer, and the measurements were made at equilibrium volumes for well-annealed samples.\*

To discuss further the observed difference between the viscoelastic behavior in the transition zone of L-1 and the remaining samples, we evaluated the retardation spectrum by using the second approximation method of Schwarzl—Staverman.<sup>13</sup> The results are shown in Figure 5 where the retardation spectrum  $L(\tau)$  of seven

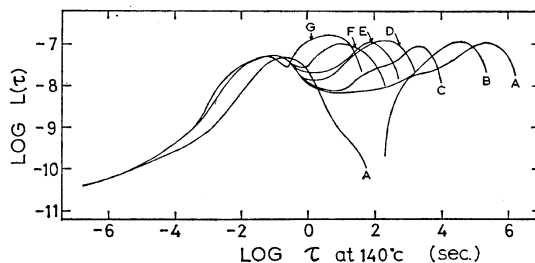


Figure 5. Retardation spectra of seven polystyrene samples. Key same as in Figure 2.

\* The measurements were made for sample L-1 annealed at 160°C for two hours and the creep curves obtained were quite close to the master curve in Figure 2.

samples are plotted logarithmically against the retardation time  $\tau$ . A shift similar to that discussed above is again observed at short retardation times; that is, the spectrum of L-1 coincides with those of other samples at  $\log \tau$  below  $-5$  and is displaced in almost parallel to longer times in the range of  $\log \tau$  from  $-5$  to about  $0$ . The maximum value of the horizontal displacement is  $0.6$  on the logarithmic time scale, which is identical to the value derived from the master curves in Figure 2. Moreover it should be noted that  $L(\tau)$  of L-1 disappears in the vicinity of  $\log \tau = 2$ , and hence is separated into two regions. The left region is associated with the retardation process of individual strands of the entanglement network and the right may be related to cooperative motions extending through large regions of the three-dimensional structure. Thus in the transition zone, L-1 behaves as if it were a permanently crosslinked polymer network in which molecular motions of individual polymer chains between crosslinking points are responsible for the whole retardation process of the polymer. In this connection, it may be noted that Maekawa, *et al.*<sup>14</sup> have reported a similar shift in the transition zone to lower frequencies with increasing crosslinking from the dynamic measurements of polybutadiene samples crosslinked by dicumyl peroxide. Moreover a constant shift factor has been used by them for all samples irrespective of crosslinking density. Therefore the shift in the transition zone of L-1 may be closely related to the separability of its  $L(\tau)$  into two regions, although the molecular origin of the shift is uncertain at present. For the viscoelastic behavior in the terminal zone which is another object of this study, however, the above discrepancy between the highest molecular weight sample and others, will not seriously affect the later discussions. Because, for all samples, the superposition procedure was performed by using shift factors of quite the same temperature-dependent nature through the transition and terminal zones.

#### Rubbery Zone and Entanglement Spacing

To examine the viscoelastic behavior in the rubbery zone, it is common to use the relaxation spectrum  $H(\tau)$ . Nevertheless qualitative

discussions are possible from  $L(\tau)$  in Figure 5. It can be seen that there is a relatively flat region, corresponding to the plateau zone of  $H(\tau)$ , for samples of molecular weight much larger than average molecular weight between entanglements (for example, L-49), but such a region does not exist for L-1. The disappearance of the plateau zone for extremely high molecular weight samples seems to imply that the plateau zone consists of two contributions—one from the distribution of the strand lengths of the entanglement network and the other from entanglement slippage at longer times. Therefore, if molecular weight is so high that the two contributions are completely separated and, in addition, there is no disturbance due to any molecular weight distribution, the plateau zone would probably vanish in  $L(\tau)$ . The above argument is supported by the recent theory proposed by Chompff and Duiser (CD theory).<sup>16,17</sup> They have shown that the relaxation spectrum  $H(\tau)$  is composed of two separate Rouse-type spectra and vanishes in the intermediate region between them. Additional evidence is that the shapes of the two maxima in the  $L(\tau)$  are almost the same and a slope of approximately  $1/2$  can be drawn on the left of both maxima. Thus the CD theory can explain the observed behavior in the rubbery state rather well but the discrepancy between theory and experiment will become clear in the terminal zone as described later.

The present measurement affords two estimates of the average molecular weight between entanglements,  $M_e$ . A rough calculation can be made from the height of the maximum in the  $L(\tau)$ <sup>12</sup> in the vicinity of  $\log \tau = 0$  by using eq 6

$$M_e = \frac{3\pi}{0.64} \cdot L_m \cdot \rho RT \quad (6)$$

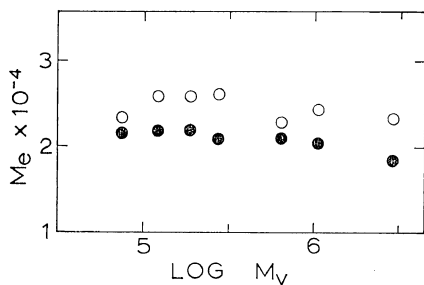
where  $L_m$  is the height of the maximum. Alternatively,  $M_e$  can be also calculated following the procedure of Tobolsky and Takahashi.<sup>17</sup> Plotting the 100 sec tensile creep compliance,  $D(100)$ , against temperature, we evaluated  $M_e$  from  $D_2$ , the value of  $D(100)$  at the inflection point in the rubbery zone of the plot, by eq 7

$$M_e = 3\rho RT_1 D_2 \quad (7)$$

where  $T_1$  is the absolute temperature at which  $D_2$  is determined. The results are all listed in Table II and Figure 6 gives the plot of  $M_e$  vs.

**Table II.** Average molecular weight between entanglements

Sample	$M_e$ from	
	Max in $L(\tau)$	Inflection in the plot of $D(100)$ vs., $T$
L-1	$2.33 \times 10^4$	$1.84 \times 10^4$
L-2	$2.43 \times 10^4$	$2.05 \times 10^4$
L-49	$2.28 \times 10^4$	$2.10 \times 10^4$
L-41	$2.60 \times 10^4$	$2.08 \times 10^4$
L-39	$2.58 \times 10^4$	$2.18 \times 10^4$
L-38	$2.58 \times 10^4$	$2.17 \times 10^4$
L-36	$2.33 \times 10^4$	$2.15 \times 10^4$



**Figure 6.**  $M_e$  plotted against  $\log M_v$  for seven polystyrene samples. White circle, from eq 6; black circles, from eq 7.

$\log M$ .  $M_e$  estimated from the maximum in  $L(\tau)$  are somewhat higher than those from the inflection in  $D(100)$ , but, if one takes account of large experimental errors involved in the former method, both are in reasonable agreement. They are independent of molecular weight as expected.

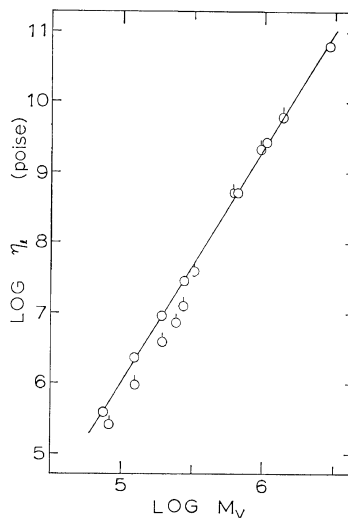
#### Terminal Zone

The viscoelastic behavior in the terminal zone is characterized by the tensile viscosity  $\eta_l$  and the steady-state compliance  $D_e$ . These quantities were calculated for all samples by employing the extrapolation method of Ninomiya<sup>18</sup> as well as by extrapolating a linear plot of the tensile creep compliance  $D(t)$  against  $t$ . The values of  $\eta_l$  and  $D_e$  estimated by both methods agreed with each other within errors of 5% and 15%,

respectively. In Table III the values calculated by the former method are given, since the former method is considered to be more reliable than the latter. In Figure 7 the values of  $\eta_l$

**Table III.** Tensile viscosity, steady-state compliance and maximum relaxation time at 160°C

Sample	$\eta_l$ , poise	$D_e$ , cm <sup>2</sup> /dyne	$\tau_m$ , sec
L-1	$6.20 \times 10^{10}$	$6.13 \times 10^{-7}$	$9.97 \times 10^4$
L-2	$2.70 \times 10^9$	$6.31 \times 10^{-7}$	$5.16 \times 10^3$
L-49	$5.13 \times 10^8$	$5.80 \times 10^{-7}$	$6.02 \times 10^2$
L-41	$2.85 \times 10^7$	$6.93 \times 10^{-7}$	$9.11 \times 10^1$
L-39	$9.15 \times 10^6$	$6.10 \times 10^{-7}$	$1.76 \times 10^1$
L-38	$2.29 \times 10^6$	$6.63 \times 10^{-7}$	$4.76 \times 10^0$
L-36	$3.83 \times 10^5$	$6.96 \times 10^{-7}$	$1.06 \times 10^0$



**Figure 7.**  $\eta_l$  at 160°C plotted logarithmically against  $M_v$ . No pip, our data; pip up, data of Akovali.<sup>6</sup>

at 160°C are plotted logarithmically against  $M_v$  which is negligibly different from  $M_w$ . It can be seen that the plot is strictly represented by a straight line with the slope of 3.3 in the whole range of molecular weights from  $7.5 \times 10^4$  to  $2.9 \times 10^6$ , which approximately conforms to the prediction of either the FLW or CD theories. Recently Tobolsky, *et al.*<sup>5</sup> and Akovali<sup>6</sup> have reported from stress relaxation measure-

ments that  $\eta_l$  of narrow-distribution polystyrene varies as  $M^{3.75-4}$ . Their data at 129°C were reduced to 160° by using their shift factor and plotted in Figure 7, for comparison. For molecular weights larger than  $3.0 \times 10^5$  their data fit our line having the slope of 3.3 very well, but for molecular weights smaller than  $2.0 \times 10^5$  their values of  $\eta_l$  are smaller than ours by about a factor of 2.2. At the present time, the reason for the discrepancy between two results is not clear. At any rate there is no such decrease in the molecular weight dependence of  $\eta_l$  as that observed for poly( $\alpha$ -methylstyrene)<sup>1</sup> in the high molecular weight region but the linear relationship between  $\log \eta_l$  and  $\log M$  seems to be realized up to very high molecular weights.

The values of  $D_e$  at 160°C are plotted logarithmically against  $M_v$  in Figure 8.  $D_e$  is almost

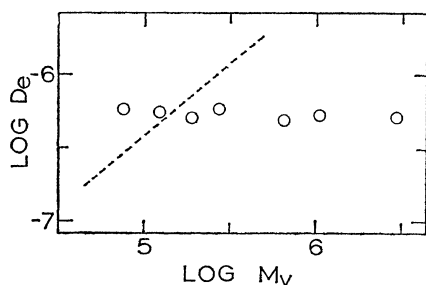


Figure 8.  $D_e$  at 160°C plotted logarithmically against  $M_v$ . Broken line represents theoretical relation.<sup>2</sup>

independent of molecular weight within the limits of experimental error. This is in contrast to the theoretical prediction<sup>2-4,15</sup> that  $D_e$  should be proportional to molecular weight. The same discrepancy was observed for some polystyrene samples in the range of molecular weights from  $8.2 \times 10^4$  to  $1.32 \times 10^6$  by Tobolsky, *et al.*,<sup>5,6</sup> though there is some scattering, and also for poly( $\alpha$ -methylstyrene) in the high molecular weight region in the previous study.<sup>1</sup> These results suggest that the steady-state compliance of narrow-distribution polymers becomes constant for molecular weights much larger than  $M_e$ . The results of the shear creep measurements on monodisperse *cis*-1,4-isoprene also

lend support to the above statement.<sup>19</sup>

It is interesting to compare the molecular weight dependence of the maximum relaxation time  $\tau_m$  with that predicted by the theories. With this objective in view, the creep master curves of Figure 2 were converted, through the use of the well-known approximate formula,<sup>20</sup> to the relaxation moduli data, from which  $\tau_m$  was calculated by using Procedure X.<sup>21</sup> The results are given in Table III. The 3.3 power dependence of  $\tau_m$  on molecular weight, as shown in Figure 9, reveals another deviation from the

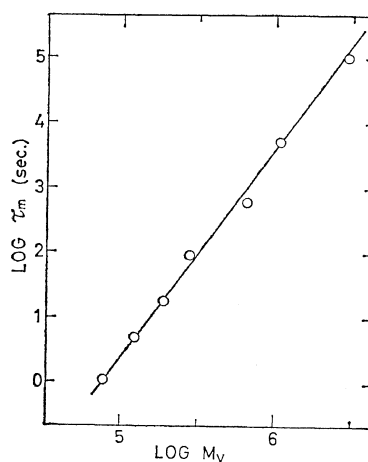


Figure 9.  $\tau_m$  at 140°C plotted logarithmically against  $M_v$ .

theories, since they predict that  $\tau_m$  should vary as the 4.4 power of molecular weight. The observed discrepancies between the theories and experimental results may be attributed to the invalidity of the assumption in the theories that entanglements affect all the long relaxation times to the same degree or, in other words, that the effective friction constant for molecular motions with nodes spaced farther apart than  $2M_e$  are affected by entanglements in the same manner as the steady-flow viscosity. Alternatively it might be considered that entanglements affect not only the friction constant  $\zeta$  but also the force constant  $k$ . This idea has been formulated recently by Hayashi.<sup>22</sup> Putting that

$$\zeta_p = \zeta_0, \quad k_p = k \quad p > \frac{M}{M_e}$$

$$\zeta_p = \zeta_0 \left( \frac{M}{pM_e} \right)^{2.5}, \quad k_p = k \frac{M}{pM_e} \quad p < \frac{M}{M_e} \quad (8)$$

where  $\zeta_p$  is the effective friction constant for the  $p$ -th mode and so on, and after solving the diffusion equation, he has obtained the steady-state compliance independent of molecular weight as well as 3.5 power dependence of  $\tau_m$  on molecular weight. These predictions are in agreement with the present results. However, his relaxation spectrum consists of the wedge-type (the slope of  $-1/2$ ) and the box-type spectrum, which is inconsistent with the retardation spectrum obtained for L-1.

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