efficient of the minor component decreases with increasing molecular weight of the major component, but when the latter is large enough, the diffusion coefficient levels out and becomes insensitive to it.[10] Chloroform, benzene, and hexamethyldisiloxane (HMS) are small molecules, and thus their diffusion becomes independent of polymer molecular weight at relatively low molecular weight. However, as the molecular weight of the minor component increases, its motion remains sensitive to the molecular weight of the other (polymer) component up to much higher values.

It is interesting to note that the increase in molecular weight of the major component to which the diffusion of the minor component is sensitive is not as great as the increase in molecular weight of the minor component itself. Whereas the ratio MW(major)/MW(minor) at the turning or leveling-off point is greater than 10 for low molecular weight of minor component, this ratio approaches unity at the highest molecular weights studied. It would be interesting to see what happens to this ratio at the turning point for a still higher molecular weight of the minor component, but the measurements made represent the limit of our capabilities with the spin-echo method.

A pictorial explanation of most of the above results can be given as follows. For two polymer molecules to become disentangled and to move out of each others' way, the entire length of the small molecule as well as a roughly equal portion of the larger molecule must move in a coordinated fashion. The motion of this portion of the larger molecule is expected to be independent of how far away the chain ends are, at least beyond a certain minimum distance. Thus the ease of motion of the smaller molecule is determined by its own size, but not by the size of the larger molecule.

On the other hand, diffusion of the large molecule is determined not only by the difficulty of disentangling from a given small molecule, but by the number of small molecules with which it is entangled. This is in turn proportional to its length. Thus the ease of diffusion of the large molecule is determined by the lengths of the chains of both components.

Acknowledgment. Thanks are due to S. J. Hoffman for performing the viscosity measurements reported here. Acknowledgment is also made of helpful discussions with R. Ullman, W. Rothschild, and J. E. Anderson.

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[10] The fact that the self-diffusion coefficient of a polymer is independent of the molecular weight of a matrix polymer when the latter is much greater has also been observed in the case of polystyrene, molecular weight 80,000, in a radiotracer study by F. Bueche, *J. Chem. Phys.*, **48**, 1410 (1968).

Studies on the Stress Relaxation of Polystyrenes in the Rubbery Flow Region. II

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ABSTRACT: An empirical equation for stress relaxation in the rubbery flow region has been applied to commercial and narrow-distribution polystyrenes. The parameters involved have been mathematically related to the shear viscosity, η_s, and steady-state shear compliance, J_e^0. Relationships between the parameters and the molecular weight averages of the samples are also presented. An extrapolation to a completely monodisperse species is performed and its implications are discussed.

In the first paper of this series,[1] the empirical time-dependent modulus equation

$$E_r(t) = E_r(0)e^{-(t/\tau)^B} \qquad (1)$$

of DeBast and Gilard[2] was presented as adequately describing the rubbery plateau, rubbery flow, and terminal regions of the time-dependent modulus of narrow distribution polystyrenes. In this three-parameter equation, $E_r(0)$ is the value of the rubbery plateau modulus, τ is the time parameter which determines the length of the rubbery plateau, and B is the rate-of-decay parameter which influences the shape of the rubbery flow region. The previous paper[1] fitted eq 1 to the experimental modulus–time curves by a least-squares technique which allowed all three parameters to vary. The result was approximately constant values for $E_r(0)$ and B, while τ was found to follow the following relation when expressed in seconds for modulus curves at 115.0°

$$\tau = (1.4 \times 10^{-14})M^{3.4} \qquad (2)$$

This relationship shows the strong molecular weight dependence of the length of the rubbery plateau region, as has been observed by others.[3,4] The shape of the rubbery flow region has been observed to be pronouncedly affected by the breadth of the molecular weight distribution. The shape determines the value of B in eq 1, which must be chosen so as to accommodate the much broader rubbery flow region observed for polydisperse samples.[5] Therefore, B would appear to be a function of the heterogeneity of the polymeric material. Of course, we are aware that a distribution of molecular weights cannot be defined by a single variable, and thus at best B might be some function of a quantity relatable to the molecular weight distribution. We must also be aware that, because we are using a single parameter, B, to describe the shape of the modulus curve, we are restricted to describing the time-dependent modulus behavior of unimodal or close to unimodal distributions of molecular weights. The work done on

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[1] M. Narkis, I. L. Hopkins, and A. V. Tobolsky, *Polym. Eng. Sci.*, **10**, 66 (1970).

[2] J. DeBast and P. Gilard, *Phys. Chem. Glasses*, **4**, 117 (1963).

[3] A. V. Tobolsky, J. J. Aklonis, and G. Akovali, *J. Chem. Phys.*, **42**, 723 (1965).

[4] S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **3**, 109 (1970).

[5] K. Ninomiya and H. Fujita, *J. Colloid Sci.*, **12**, 204 (1957).

TABLE I

Sample	$\bar{M}_N{}^a$	$\bar{M}_w{}^a$	HI[a,b]	B	Log τ^d	Log $\eta_t{}^e$	Log $\eta_t{}^f$
S102	78,500	82,500	1.05	0.622	3.13	9.95	9.98
S103	118,000	124,700	1.05	0.608	3.78	10.60	10.62
	109,000	117,000	1.07				
S109	182,000	193,000	1.06	0.579	4.32	11.17	11.21
	167,000	179,000	1.07				
S111	221,000	239,000	1.08	0.570	4.56	11.42	11.45
	200,000	217,000	1.08				
S108	247,000	267,000	1.08	0.495	4.60	11.57	11.68
	236,000	242,000	1.03				
5A		450,000[c]		0.650	5.68	12.49	12.47
4A		100,000[c]		0.640	3.47	10.25	10.27

[a] First value is from ref 8, second from ref 9. [b] HI = $\bar{M}_M/\bar{M}_N$. [c] Determined by Koppers, Inc. [d] τ in seconds at 115°. [e] η_t in poise at 115° from eq 4. [f] η_t in poise at 115° from eq 3.

TABLE II

Sample	$\bar{M}_N{}^a$	$\bar{M}_w{}^a$	HI[b]	B^c	Log τ^c	$\bar{M}_v$	Log $\eta_t{}^d$	Log $\eta_t{}^e$
SP187	100,000	249,000	2.49	0.277	3.69	218,000	11.46	11.38
SP185	100,000	253,000	2.53	0.275	3.68	220,000	11.47	11.41
SP184	85,000	210,000	2.46	0.288	3.38	185,000	11.08	11.13
SP186	88,000	204,000	2.31	0.330	3.40	180,000	10.82	10.85
2892-55	141,000	282,000	2.00	0.322	4.06	269,000	11.52	11.53
D9	108,000	227,000	2.10	0.315	3.70	200,000	11.16	11.16

[a] Determined by gel permeation chromatography by Koppers, Inc. [b] HI = $\bar{M}_w/\bar{M}_N$. [c] τ in seconds at 115°. [d] η_t in poise at 115° from eq 4. [e] η_t in poise at 115° from eq 3.

binary blends of narrow-distribution polystyrenes has shown that step-type rubbery plateau regions are obtained.[6,7] It is obvious that eq 1 with its single parameter B would be unable to describe such behavior. The approximate molecular weight independence of $E_r(0)$, the rubbery plateau modulus, has been observed elsewhere,[3,4] and if the restrictions mentioned above are adhered to, we would expect $E_r(0)$ to be independent of both molecular weight and the distribution of molecular weights. We present here a more careful analysis of the available data on narrow-distribution polystyrene and an extension of the applicability of eq 1 to a series of commercially available polystyrenes with distributions of molecular weights in the random-distribution range.

Experimental Section

The narrow distribution samples, Table I, used here are mainly the extensively characterized Dow Chemical Co. series.[8,9] The time-dependent modulus data are those obtained by Aklonis and Tobolsky.[10] The data have been shifted to 115.0° using the experimental shifting factors included in that paper. The commercially prepared polystyrenes, Table II, were supplied by Koppers Co. Inc. Molecular weight averages have been obtained from gel permeation chromatography data which have been corrected for axial dispersion effects.[11] Viscosity-average molecular weights were also determined experimentally in benzene at 25° by using the equation[12]

$$\bar{M}_v = \left(\frac{[\eta]}{1.13 \times 10^{-4}}\right)^{0.73}$$

The time-dependent moduli of the commercial polystyrenes were measured at several temperatures and shifted using time–temperature superposition to a single curve at 115.0°. The additional narrow-distribution samples 5A and 4A are Pressure Chemical samples and were tested in the same manner as the commercial samples.

The procedure for fitting eq 1 to the experimental modulus curves was extensively modified in order to avoid some mathematical difficulties in the three-parameter least-squares technique and to include more of the experimental data. The new procedure involved first, by preliminary fitting, the selection of a value for $E_r(0)$. The best value for all the samples studied here was

$$E_r(0) = 4.41 \times 10^6 \text{ dyn/cm}^2$$

Once this has been established, the value of τ is merely the time, t, at which $E_r(t)$ had decayed to $E_r(0)/e = 1.63 \times 10^6$ dyn/cm^2. B was then determined by an iterative least-squares method.

Results and Discussion

Figures 1 and 2 indicate the fits of eq 1 to the rubbery flow regions of the narrow- and commercial-distribution samples, respectively. The values of B and τ necessary to produce this fit are included in Tables I and II. The poorer fit for samples S109, S111, and S108 can be traced to the fact that the assumed value of $E_r(0)$ is not the optimal one for these samples. A procedure X[13] determination of the exponential coefficients for these samples indicates that a better value of $E_r(0)$ would be slightly less than that assumed. The assumption of constancy of $E_r(0)$ was preferable to a slightly better fit.

In order to test more quantitatively the fit of eq 1 and to develop further the consequences of its use, we can consider the following expression for the tensile viscosity.

$$\eta_t = \int_0^\infty E_r(t)\mathrm{d}t \qquad (3)$$

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(6) T. Masuda, K. Kitagawa, T. Inoue, and S. Onogi, *Macromolecules*, 3, 116 (1970).

(7) G. Akovali, *J. Polym. Sci., Part A-2*, 5, 875 (1967).

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(11) M. Hess and R. F. Kratz, *J. Polym. Sci., Part A-2*, 4, 731 (1966).

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(13) A. V. Tobolsky, "Properties and Structure of Polymers," Wiley, New York, N. Y., 1960, p 188.

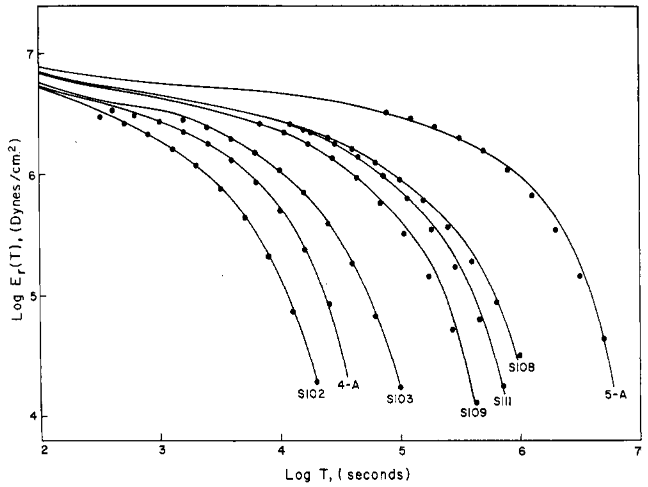

Figure 1. Long-time region of the relaxation modulus for the narrow-distribution samples at 115.0°. The solid line indicates the experimental data. Points have been calculated by using eq 1 with values of B and τ indicated in Table I.

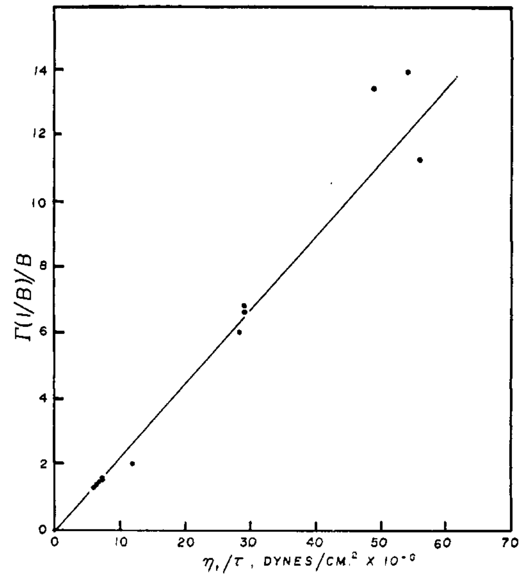

Figure 3. $\Gamma(1/B)/B$ as a function of η_t/τ. τ is in seconds at 115.0°. η_t is in poise at 115.0° calculated by numerical integration of eq 3. The line drawn is that of eq 4.

Because eq 1 covers the portion of the relaxation modulus curve which accounts for essentially the entire value of this integral, substitution into eq 3 is valid. Upon integration, we obtain[1]

$$\eta_t = \frac{\Gamma(1/B)}{B} E_r(0)\tau \qquad (4)$$

Comparison of the values of the tensile viscosity calculated from B and τ using eq 4 with those obtained by direct numerical integration of eq 3 provides an idea of the fit obtained. These values have been included in Tables I and II.

It is also helpful to plot η_t (from eq 3)/τ *vs.* $\Gamma(1/B)/B$. This has been done in Figure 3. The line drawn is that predicted by eq 4 with a slope of $1/E_r(0)$. How well the points follow the line is a measure of the fit. We see that the ability of eq 1 to simulate the experimental data decreases somewhat for the largest values of η_t/τ encountered here, but is very satisfactory for the lower and intermediate values.

The Characteristic Relaxation Time, τ. The values of τ were found to follow a 3.4-power law with the number-average molecular weight for all the samples studied irrespective of heterogeneity. Figure 4 is a double logarithmic plot of this characteristic relaxation time *vs.* $\bar{M}_N$, the number-average molecular weight. The line drawn to approximate the relationship can be described by the following equation.

$$\tau \text{ (sec, 115°C)} = (3.04 \times 10^{-14})\bar{M}_N^{3.4} = K\bar{M}_N^{3.4} \qquad (5)$$

The most significant aspect of this relationship is that the short-time portions of these curves are uniformly controlled by the number-average molecular weight in the range of distributions studied. Of course, as the distributions become much wider, with the inclusion of significant amounts of low molecular weight species, this general relationship will probably fail. This aspect is now being studied with a series of broad-distribution, $\bar{M}_w/\bar{M}_N > 3.0$, low molecular weight, $\bar{M}_N \simeq 50{,}000$ polystyrenes.

Viscosity and the Rate of Decay Parameter, B. Now that the molecular weight dependence of τ has been established, we can substitute eq 5 into eq 4 to obtain

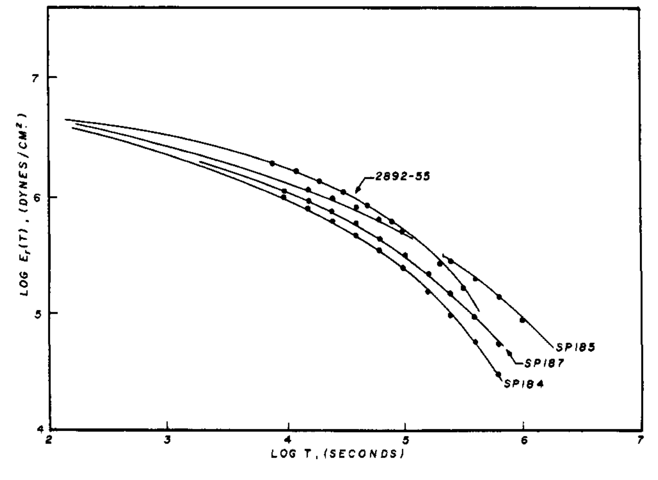

Figure 2. Long-time region of the relaxation modulus for four of the commercial polystyrenes at 115.0°. The solid line indicates the experimental data. Points have been calculated by using eq 1 with values of B and τ indicated in Table II.

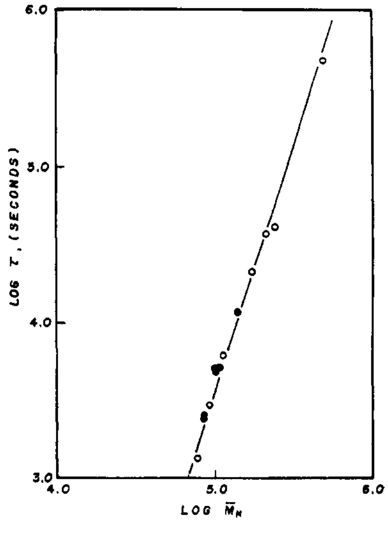

Figure 4 Logarithm of τ as a function of the logarithm of $\bar{M}_N$ at 115.0°. The line drawn is that of eq 5.

$$\eta_t = \frac{\Gamma(1/B)}{B} E_r(0)K\bar{M}_N^{3.4} \tag{6}$$

We see that the variation of the rate of decay parameter, B, or in this case, $\Gamma(1/B)/B$, necessarily is involved with the molecular weight dependence of the viscosity.

In the power laws, which are generally used to describe bulk viscosity of polymers, the points of continuing interest are the molecular weight average to be used and the power to which it is raised. Many investigators of wide varieties of bulk polymeric systems have generally found that the weight average or a solution viscosity average is most satisfactory.[3,4,6–9,14–16] The various powers to which these molecular weights are raised range from 3.14[8] to around 3.7[4,6] with many centered around the often-mentioned value of 3.4.[9,14–16] In one instance, a value of 4.0 has been reported.[3]

On the strictly theoretical side, a few have been able to duplicate the experimentally found power law by considering the mechanics of the entangled polymer system.[17,18] The problem of heterodispersity has also been treated and predicts that a molecular weight average slightly above $\bar{M}_w$ is proper in a power law.[18–20] This has never been experimentally verified and in fact more experimental evidence, including that presented here, points to an average slightly less than the weight average rather than one higher. The predictions of the theories are most reasonable, however, if one considers the approximations necessary to treat this system.

Figure 5 is a double logarithmic plot of the tensile viscosity in poise at 115° *vs.* molecular weight. In order to get both the narrow-distribution samples and the commercial samples to follow a single expression, it was necessary to use the viscosity-average molecular weights. In the case of the narrow-distributions samples, $\bar{M}_w$ being experimentally indistinguishable from $\bar{M}_v$, the line drawn can be expressed by the following equation

$$\eta_t\,(\text{P}, 115°) = (1.74 \times 10^{-7})\bar{M}_v^{3.4} = K'\bar{M}_v^{3.4} \tag{7}$$

Combining this equation with (6), we see that the function $\Gamma(1/B)/B$ follows the following expression

$$\frac{\Gamma(1/B)}{B} = \frac{K'}{E_r(0)K}\left(\frac{\bar{M}_v}{\bar{M}_N}\right)^{3.4} \tag{8}$$

for the experimental data presented here.

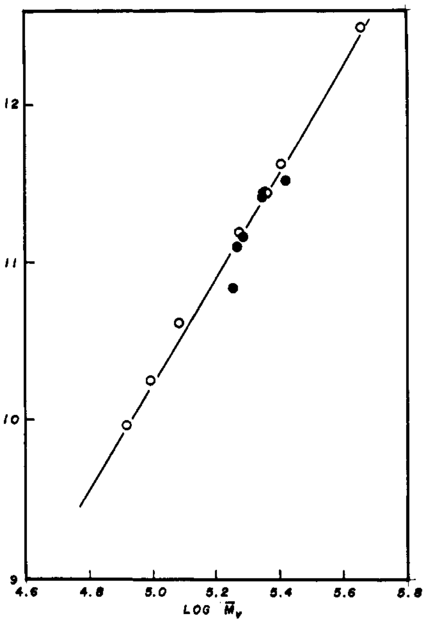

Figure 5. Logarithm of η_t as a function of the logarithm of $\bar{M}_V$ at 115.0°. The line drawn is that of eq 7.

The Monodisperse Species. Because eq 6, 7, and therefore 8 are apparently experimentally valid for unimodal distributions of molecular weights with $\bar{M}_v/\bar{M}_N$ values of 1.05 to approximately 2.0, the extrapolation of (7) to a single monodisperse species of polystyrene is possible. For the monodisperse spectra $\bar{M}_v/\bar{M}_N = 1.00$ and

$$\frac{\Gamma(1/B')}{B'} = \frac{K'}{KE_r(0)} = 1.2 \tag{9}$$

where B' is the value of B for this as of yet synthetically unobtainable entity. The solution of eq 9 for B' yields a value of 0.75. With this value for B', we may now predict the form of the relaxation modulus for a perfectly monodisperse polystyrene sample, and express it in the following manner

$$E_r(t) = E_r(0)e^{-(t/\tau)^{0.75}} \tag{10}$$

where

$$\tau = KM^{3.4}$$

Figure 6 shows the form of the relaxation modulus in the terminal region as predicted by eq 10. The curve for a typical narrow-distribution polystyrene, with $B = 0.60$, has been included for comparison. It is clear that these two materials would be experimentally distinguishable. Figure 7 shows the predicted distributions of relaxation times, $H(\tau')$, which are necessary in the viscoelastic equation

$$E_r(t) = \int_{-\infty}^{+\infty} H(\tau')e^{-(t/\tau')}\mathrm{d}(\ln \tau') \tag{11}$$

in order to reproduce the relaxation modulus curves of Figure

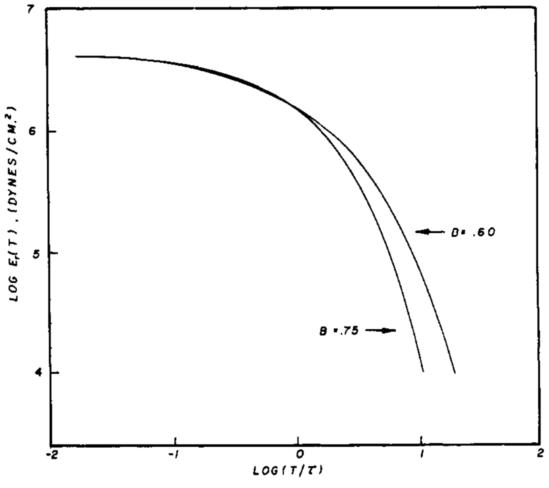

Figure 6. The predicted relaxation modulus curves for a typical narrow-distribution polystyrene and completely monodisperse polystyrene.

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(15) K. Ninomiya, *J. Colloid Sci.*, **17**, 759 (1962).
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(18) W. W. Graessley, *ibid.*, **47**, 1942 (1967).
(19) F. Bueche, *J. Polym. Sci.*, **43**, 527 (1960).
(20) W. W. Graessley, *J. Chem. Phys.*, **54**, 5143 (1971).

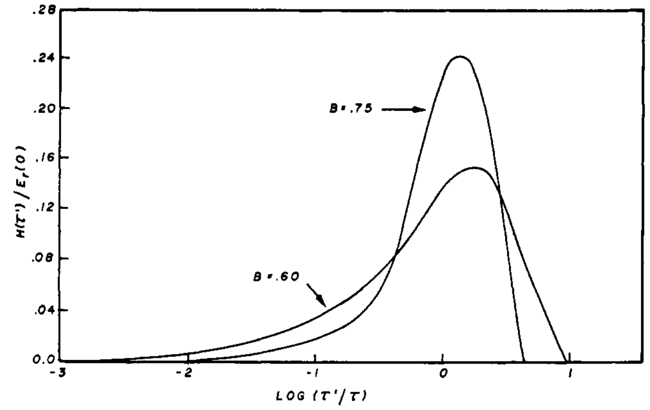

Figure 7. The predicted distribution of relaxation times for a typical narrow-distribution and a completely monodisperse polystyrene.

6. Both the distributions of relaxation times were calculated by an iterative second approximation method.[21]

We believe that this projected form of the distribution of relaxation times for a single polystyrene species can be very helpful in predicting the viscoelastic properties of heterodisperse materials.

Steady-State Shear Compliance, J_e^0. An expression for the steady-state shear compliance can also be obtained by substituting (1) into

$$J_e^0 = \frac{3}{\eta_t^2}\int_0^\infty tE_r(t)\mathrm{d}t \qquad (12)$$

and integrating over time. This procedure produces

$$J_e^0 = \frac{3\Gamma(2/B)B}{[\Gamma(1/B)]^2E_r(0)} \qquad (13)$$

Because of the appearance of the expression $\Gamma(2/B)$, it is obvious that J_e^0 cannot be expressed as any simple function of the molecular weight averages used here. However, within the range of validity of eq 1 shown by Figure 3, we can use eq 8 and 13 together to predict values of J_e^0. This is done with the understanding that this is subject to all the restraints with which eq 1 has been applied. Figure 8 shows the predicted variation of J_e^0 with $\overline{M}_V/\overline{M}_N$.

A further aspect of the steady-state shear compliance can be seen by substituting B' into (13) which results in

$$J_e^0 = 1.42/(E_r(0)/3) \qquad (14)$$

It is noteworthy that Graessley's theoretically predicted value of J_e^0 for "infinite" molecular weight is $1.79/(E_n(0)/3)$. Also Graessley's predicted values of J_e^0 are very slowly varying functions of the molecular weight in the region 100,000–500,000. It is not impossible that our values of B' are also a very slowly varying function of molecular weight in this same range; if this is true, our experimental results are not sufficiently sensitive to detect it.

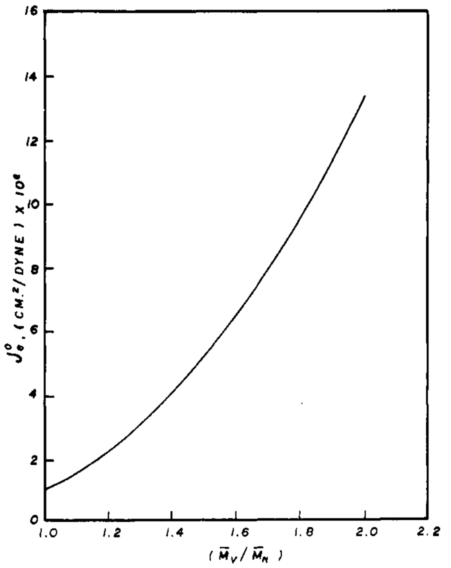

Figure 8. The variation in J_e^0 with $\overline{M}_V/\overline{M}_N$ as predicted by eq 8 and 14.

Summary

Stress relaxation of both narrow-distribution and commercially available polystyrenes in the rubbery flow region may be characterized by the three-element equation

$$E_r(t) = E_r(0)e^{-(t/\tau)^B}$$

To a good approximation, $E_r(0)$ is 4.41 × 10^6 dyn/cm^2, while τ is proportional to $\overline{M}_N{}^{3.4}$. The exponent B is a function of the breadth of distribution of molecular weights. Specifically, $\Gamma(1/B)/B$ can be simply related to the variation of the bulk viscosity, η_t, with molecular weight. Using the resulting expressions, the relaxation modulus and relaxation time distribution for a perfectly monodisperse polystyrene can be predicted. Further, the resulting expression for J_e^0 allows its prediction with a minimum information and also correlates well with a molecular entanglement theory.

Acknowledgments. We should like to acknowledge the assistance of Dr. R. Kratz and Dr. E. M. Fettes of Koppers, Inc., for supplying samples, molecular weight information, and for much useful discussion. The partial support of the Office of Naval Research is gratefully acknowledged.

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