

Comparison of Similar Narrow Molecular Weight Polystyrenes

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Synopsis

Discrepancies between the level of the viscosity at 200°C of the Dow series of polystyrenes and another narrow molecular weight distribution polystyrenes have been pointed out by Toosi, Porter, and Johnson in 1969. Penwell and Graessley have shown in 1974 that over a wide range in temperature one member of this series, S109, has a significantly lower viscosity than samples of similar molecular weight from other sources. Fetters has established the presence of high molecular weight tails in several of the much studied series. The investigation being reported here reveals the effect of the high molecular weight tail in the viscoelastic behavior of the S109 in the terminal zone of response. In addition, it is shown by an enhanced rate of creep in the glass to rubber-like dispersion that the glass temperature of the S109 is depressed by about 4°C.

INTRODUCTION

Before the advent of the direct preparation of narrow molecular weight distribution polymers by means of anionic polymerization without termination (i.e., the "living polymer" method), the only means to obtain specimens with moderately narrow distributions was fractionation by coacervation or column elution. The best samples prepared by the fractionation techniques were estimated to have heterogeneity indices (M_w/M_n) no better than 1.1 or 1.2, where M_w is the weight-average and M_n is the number-average molecular weight. Anionically polymerized polystyrenes and polybutadienes were thought to offer narrower distributions, with M_w/M_n ratios less than 1.05, perhaps approaching 1.01. Quite often, they have been optimistically referred to as being "monodisperse." The availability of large amounts of very narrow-distribution polymers inspired many investigations where previously quantities were too limited for them to be considered or where the molecular weight dependence of a property was in doubt because of a greater sensitivity of the property to the molecular weight distribution, MWD, than to the molecular weight itself.¹ The measurement of engineering properties is an example of the former, and the viscoelastic response in the terminal zone is an example of the latter. Many valuable results have been obtained in the study of these polymers. However, we wish to join the growing call for caution in assuming that the anionically polymerized polystyrenes are all of equal quality.

Toosi, Porter, and Johnson² pointed out in 1969 that the Dow series of polystyrenes were reported by nine groups of investigators to exhibit viscosities at

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200°C that were between two to three times lower than those reported by other investigators for polystyrenes of varied origin at corresponding molecular weights. The differences were suggested to be caused by variations in the values of different molecular weight moments that were reported. Viscosity-average molecular weights, M_v , were reported in some of the earlier studies; and because of the suspected breadth of the specimens studied, it was thought that these were substantially lower than the desired weight averages. However, it is known³ that some of the "other" polystyrenes studied were fractions of anionic polystyrenes including some of the Dow series. Unfortunately, the situation was clouded by some uncertainty in the intrinsic viscosity-molecular weight relationships.

In a 1971 review, Casale, Porter, and Johnson⁴ held to the view that molecular weight uncertainties are responsible for the viscosity molecular weight discrepancy between the Dow series and other polystyrenes. Nevertheless, in 1974 Penwell and Graessley⁵ reported that a compilation of the viscosity determinations made on the Dow S109 polystyrene with an $M_w = 1.8 \times 10^5$ over a wide range of temperatures reveals values that are approximately a factor of 2 lower than those reported for other comparable polystyrenes. The explanation advanced is that the glass temperature T_g of the S109 sample is approximately 9°C lower than that of other polystyrenes with approximately the same M_w . Since T_g is a function of the number-average molecular weight M_n , a low molecular weight tail or nonvolatile impurity would have to be present in the S109.

Subsequently, Professor Graessley encouraged Professor L. J. Fetters at the University of Akron and us to investigate the character of the Dow S109 polystyrene. Professor Fetter's primary investigatory tool is a seven-column Waters Ana-Prep gel permeation chromatograph, and ours is a frictionless torsional creep apparatus. Because the Dow series along with the polystyrenes produced by the Pressure Chemicals Co. (Pittsburgh, Pa. 15201) have been the most commonly used standards for the polymer world, Fetters and McIntyre not only have studied and reported on the S109⁶ but have carried on to investigate the detailed character of other members of the Dow series.⁷

EXPERIMENTAL

The Dow S109 polystyrene was provided to us by Professor W. W. Graessley and was studied as received and after fractionation by coacervation. The "as received" material was studied under nitrogen to reduce degradation at high temperatures. Measurements were not made under vacuum conditions to avoid the loss of any volatiles that might have been present.

A head and tail fractionation was made using benzene as the solvent and methanol as the nonsolvent. The material from the heart cut was studied in the hope that the bulk of any low molecular weight tail and plasticizing impurities might be eliminated.

Creep and creep recovery measurements were made in a torsional creep apparatus which employs a magnetic levitation bearing to eliminate the effects of friction.⁸ All measurements were made in the linear range of viscoelastic response. Viscosities were calculated from the terminal creep velocities preceding recovery measurements. Special checks for a rate-dependent viscosity were made as the glass temperature T_g was approached from above. At some temperatures, the stress level and hence the shear rate was varied by more than a

factor of 10. It had been brought to our attention that in spite of rates of shear less than 10^{-5} or 10^{-6} sec $^{-1}$ it is not safe to assume that η , the limiting low rate of shear viscosity, is being determined.⁹ Linearity tests were performed, probably for the first time, at a viscosity level of greater than 10^{12} poises (10^{11} Nsm $^{-2}$). No rate dependence was observed up to maximum stresses in the polymer of about 2×10^4 dynes/cm 2 .

RESULTS AND DISCUSSION

Recoverable Compliance Measurements

The recoverable compliance $J_r(t)$, in cm 2 dyne $^{-1}$, of the S109 polystyrene was measured directly at seven temperatures between 102° and 173°C (see Fig. 1):

$$J_r(t) = J(t) - t/\eta = J_g + J_d\psi(t)$$

where $J(t)$ is the shear creep compliance which is a function of time (t in sec), η is the shear viscosity (in poises); J_g is the "instantaneous" glassy compliance; J_d is the steady-state delayed recoverable compliance; and $\psi(t)$ is the monotonically increasing retardation function whose value is 0 at $t = 0$ and is equal to 1 at $t = \infty$. The term t/η is the measure of the permanent deformation accumulated during creep. The steady-state recoverable compliance J_e is equal to $J_g + J_d$.

The $J_r(t)$ curves were shifted along the logarithmic time scale axis to obtain a composite curve which was reduced to the reference temperature $T_0 = 100^\circ\text{C}$. No magnitude (vertical) correction was made since it appears to be unnecessary for bulk amorphous polymers in the normally accessible temperature range of measurement.¹⁰ The resulting reduced $J_r(t)$ curve is presented in Figure 2 along with the similar curve for a previously measured fraction of an anionically polymerized polystyrene designated as L-2.¹¹ The molecular weight M_v of L-2 is 1.89×10^5 , which is slightly above that of S109. The relation used in calculating M_v is

$$[\eta]_\theta = 8.5 \times 10^{-4} M_v^{1/2}$$

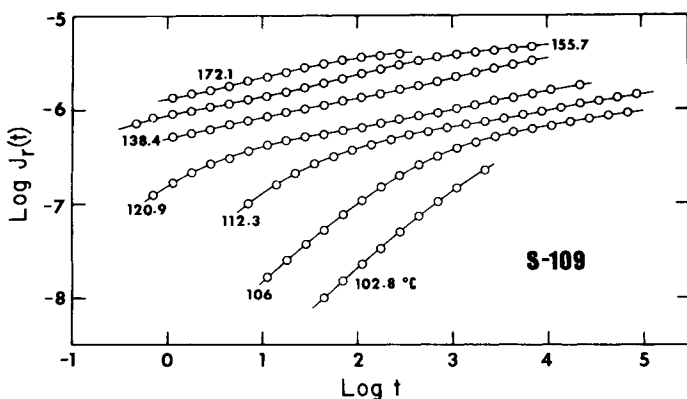


Fig. 1. Logarithmic plot of recoverable shear creep compliance $J_r(t)$, in cm 2 /dyne, for the Dow polystyrene S109 as a function of time, in sec, at seven temperatures.

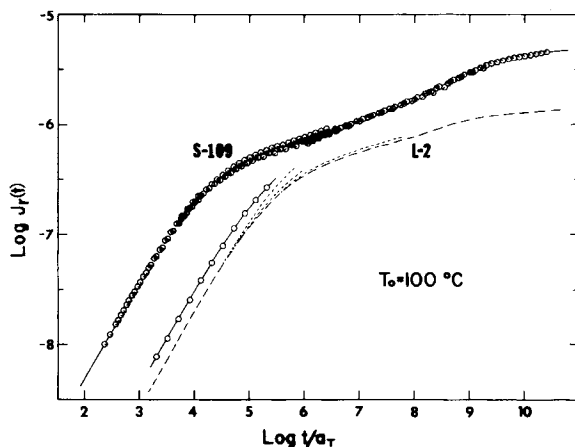


Fig. 2. Logarithmic plots of reduced $J_r(t)$ curve for S109 and L-2 as a function of the reduced time scale. Reference temperature $T_0 = 100^\circ\text{C}$. Temperatures: (\ominus) 102.8°C with 45° clockwise rotations for each successively higher temperature for S109 (whole); (\circ) S109 (fraction) at 106.0°C .

where the theta solvent is cyclohexane at 34.5°C ; $[\eta]_\theta$ for L-2 is 0.369 dl/g. Since Fetters⁶ reports $[\eta]_\theta = 0.35$ for S109, $M_v = 1.69 \times 10^5$. If we use these M_v values to compare these two polystyrenes, the ambiguities alluded to by Toosi, Porter, and Johnson² will not exist. Perhaps it is worthwhile at this point to digress to explain that the choice of M_v to characterize polymer samples with narrow molecular weight distributions is not merely motivated by convenience. Any given absolute determination of a molecular weight by light scattering or osmotic pressure cannot be expected to have much less than a 5% error. The measurement of the intrinsic viscosity can be made to be precise to about 1%. Once the Mark-Houwink relationship for a polymer solvent pair is determined, greater precision is available for other investigations where molecular weight is a variable. Random errors tend to cancel in the establishment of the relationship; and if in addition a theta solvent is used, the molecular weight exponent of $1/2$ increases the precision by a factor of 2. These factors can therefore lead to results that are possibly an order of magnitude more reproducible.

It can be seen in Figure 2 that the temperature reduction process has not been completely successful for either polystyrene. The lower-temperature curves deviate systematically from a high-temperature envelope. We have seen this faster rise of the lower-temperature curves in the response of all polystyrene samples that we have measured¹² where the molecular weight is appreciably above 1.0×10^5 .

This comparison of the reduced data shows two facts unambiguously.

1. S109 has a lower T_g than L-2 since the position of the primary or softening dispersion is found at shorter times. The top half of this dispersion is seen between $\log t/a_T = 2$ and 5 for S109 and between $\log t/a_T = 3$ and 6 for L-2. The shape of this dispersion is independent of molecular weight for samples with $M > 5 \times 10^4$, and its position is determined by the T_g of the polystyrene and hence its number-average molecular weight M_n if it is not plasticized by some solvent or contaminant. The rubber-like plateau, though not extensive, is apparent at the level $\log J_r(t) = -6.2$ for both samples in Figure 2.

2. S109 has a high molecular weight tail. This is revealed by the more ex-

tensive terminal dispersion leading to a J_e that is more than three times greater than that for L-2 which is typical of not only all the narrow-MWD polystyrenes with $M \geq 10^5$ but for nearly all the linear amorphous polymers for which it has been determined. This almost universal value is $\log J_e = -5.85(\pm 0.05)$.¹³ The presence of the high molecular weight has been directly shown by Fetters and McIntyre to be not only present in the DOW S109 but in several other members of the series.^{6,7}

Temperature Dependence

The question remains whether the value of the T_g of S109 is sufficient reason to account for the viscosity difference that is displayed in Figure 3. The solid lines are taken from Figure 1 of reference 5. Our additional data allow us to enhance the range of the viscosity covered and make it clear that the difference seen does not reflect a constant ratio of viscosities but suggests a constant temperature difference. At 200°C the viscosity of L-2 is twice as great as that of S109, and at 100° the ratio increases to a factor of 4. This changing ratio can be seen by examining the values of $\log \eta$ for both samples listed in Table I along with the time scale shift factors a_T obtained from the reduction of the recoverable compliance curves. The temperature dependence of the viscosity differs from that of the recoverable compliance¹⁴ and therefore must be analyzed separately. All the data listed were fitted to the usual free volume relationship¹⁵ using the Vogel equation¹⁶:

$$\eta \text{ (or } a_T) = A \exp [C/(T - T_\infty)]$$

where $a_T = 1$ at $T_0 = 100^\circ\text{C}$ and A , C , and T_∞ are characterizing constants whose values are given in Table II. The results of the curve fitting for the S109 data

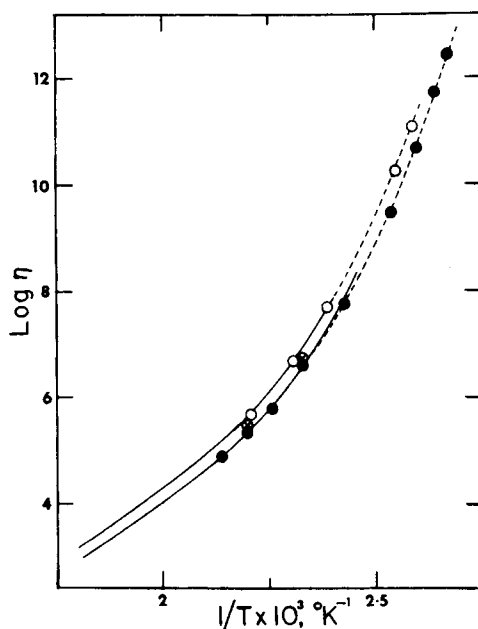


Fig. 3. Logarithm of the viscosity as a function of the reciprocal absolute temperature, in °K: (○) L-2; (●) S109 (whole); (⊗) S109 (fraction). Solid lines from reference 5.

TABLE I
 Temperature Dependences^a

$T, ^\circ\text{C}$	S109		L-2	
	$\log \eta$	$\log a_T$	$\log \eta$	$\log a_T$
100.7	—	—	—	-0.22
102.0	12.73	—	—	—
102.9	—	-0.76	—	-1.07
105.1	—	—	—	-1.76
106.0	11.73	-1.56	—	—
109.4	—	—	—	-2.67
112.3	10.67	-3.70	—	—
113.7	—	—	11.08 ₅	-3.81
116.0	—	—	—	-4.21
119.7	—	—	10.24 ₄	-4.83
120.9	9.48	-3.81	—	—
138.4	7.76	-5.22	—	—
144.9	—	—	7.70 ₀	—
155.7	6.59	-6.33	—	—
160.3	—	—	6.65 ₇	—
170.0	5.77	-6.99	—	—
180.3	5.35	—	5.66 ₅	—
193.6	4.88	—	—	—

^a Reference temperature $T_0 = 100^\circ\text{C}$.

 TABLE II
 Vogel Equation Constants^a

	S109		L-2	
	η	a_T	η	a_T
$\log A$	-0.63	-10.39	-0.46	-12.55
C	1986	814	1994	896
$T_\infty, ^\circ\text{C}$	36	66	38.7	69

^a Using the Vogel constants presented above for the viscosity of L-2 and the expression $\Delta H_{\text{app}} = CRT^2/(T - T_\infty)^2$, the apparent heat of activation ranges from 147 kcal at 100°C down to 34 kcal at 200°C . The corresponding values for the recoverable compliance of L-2 are 258 and 23 kcal. Reference temperature $T_0 = 100^\circ\text{C}$.

can be seen in Figure 4. Corresponding curves for L-2 have been previously published.¹¹ Reasonable fits are therefore obtained with the corresponding T_∞ values for S109 being 3°C lower than those for L-2. However, these differences do not constitute the most sensitive tests since the uncertainty in T_∞ can be several degrees for scattered data. Once a reasonable temperature dependence equation is available for $J_r(t)$, the temperature decrease necessary to shift the primary dispersion of S109 to superpose with that of L-2 can be calculated with appreciable certainty. The necessary shift indicated in Figure 2 is $\Delta \log a_T \approx 1.3$, which corresponds to a 3.8°C decrease in temperature.

Standard Narrow Distribution Polystyrene (NBS) 705

Fetters found that the NBS 705 polystyrene is indistinguishable from the S109 polystyrene by his gel permeation chromatographic measurements.⁶ He has also traced the history of the standard back to the Dow Chemical Co. records which indicate that the NBS 705 may in fact be the same polymer batch as Dow

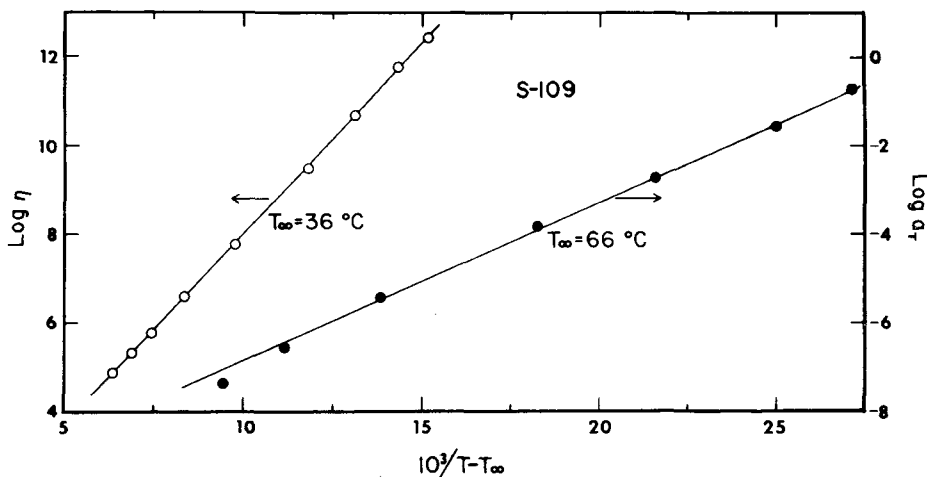


Fig. 4. Vogel temperature plots of viscosity η and recoverable compliance shift factors a_T for polystyrene S109 (whole).

S109. Fetters is convinced that they are the same. We are also convinced by the evidence and would like to refer to additional substantiating information that was obtained by Lyle Chandler¹⁷ of the Goodrich Chemical Co. on a highly reliable differential thermal analysis apparatus. Under what one believes to be the same cooling and heating histories values of 98° and 104°C for the T_g 's of the NBS 705 and PC-14a* samples, respectively, were obtained. The heating rate was 1.0°C/min. Allowing for a possible uncertainty of $\pm 1^\circ\text{C}$ in T_g , this difference is in agreement with our 4°C figure for the depression of the T_g of S109.

Fraction of Dow S109

To add substantiating evidence to the contention that the T_g of S109 is anomalously low, it was desirable to "clean" it up by attempting to remove the plasticizing moiety. A head and tail trimming was carried out, and the second fraction, or heart cut, was measured to establish the position of its primary softening transition and to determine its viscosity at a couple of temperatures. The open circles shown in Figure 2 depict the recovery response measured at 106°C and reduced to the reference temperature of 100°C. It is manifestly clear that the rough fractionation succeeded in bringing the effective M_n of S109 very close to that of L-2.

The viscosity values of the heart cut measured at 156.0° and 181.8°C are shown in Figure 3 as crossed circles. They are indeed higher than those for the whole polymer, but as seen in Table III they are not in close agreement with the values for L-2. If we assume that the heart cut has close to the same M_w as the whole polymer and that $M_v = M_w$ for these narrow distribution polymers, we can calculate the expected viscosity differences from¹⁸

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

Therefore, since $\log [\eta(\text{L-2})/\eta(\text{S109})] = 3.4 \log [M(\text{L-2})/M(\text{S109})]$ and the M_v 's

* Pressure Chemicals Co. Lot 14a, $M_w = 1.8 \times 10^6$.

TABLE III
 Comparison of Viscosities^a

T, °C	log η		log η		log η
	S109 (whole)	(0.18)	S109 (fraction)	(0.18)	L-2 (fraction)
156.0	6.56	(0.18)	6.74	(0.18)	6.92
181.8	5.29	(0.18)	5.47	(0.12)	5.59

^a Differences shown in parentheses.

are 1.89×10^5 and 1.69×10^5 for L-2 and S109, respectively, the $\Delta \log \eta$ should be equal to 0.17, which is in agreement with the difference found (see values in parentheses in Table III).

CONCLUSIONS

Our examination of the Dow S109 polystyrene has confirmed the claim of Penwell and Graessley that the viscosity of the S109 is lower than that of other narrow distribution polystyrenes with apparently the same M_w and that, in fact, its effective M_n is lower than believed, resulting in an anomalously low T_g . We disagree only in that we think that the depression of T_g is about 4°C and not 9°C as was deduced from the analysis of compiled data. In addition, the recoverable compliance behavior is in accord with the presence of the high molecular tail found by Fetters. Since Fetters found no evidence of a low molecular tail and since the T_g corresponds to an effective M_n of 2.6×10^4 ($T_g = 98.0 - 1.02 \times 10^5/M_n$; determined by T. Altares), it is most probable that a plasticizing impurity is present in the whole polymer. The fractionation process appears to remove it. Such T_g depressions encountered in the past have been attributed to contamination of the polymer by laboratory stopcock grease through handling during its reclamation from solution.

Finally, we wish to make clear that it is not suggested that the Dow series of polystyrenes is necessarily any worse than any other preparations. There are a number of documented cases of highly unexpected results^{11,19} due to the presence of molecular weight tails in low molecular weight polystyrenes that could have been misleading. It is our opinion that all anionically polymerized narrow distribution polymers should be treated with suspicion in this regard until proven to be well behaved. Unfortunately, in many cases fractionation will be necessary before reliable results will be obtained. Indeed, we believe that we have encountered cases where fractionation did not appear to eliminate effects thought to be caused by the presence of a high molecular weight tail.

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