

An Examination of the Dow and NBS 705 Polystyrene Standards Via Gel Permeation Chromatography

L. J. FETTERS, *Institute of Polymer Science, The University of Akron, Akron, Ohio 44325*

Synopsis

An examination of the molecular weight distribution via gel permeation chromatography of the Dow S-109 and NBS 705 polystyrenes has revealed that these two samples are the same. Within experimental error, both polystyrenes possess identical number- and weight-average molecular weights. In addition, the molecular characteristics of the Dow S-102, Dow S-105, Dow S-108, and Dow S-111 polystyrenes were determined. Of the samples examined, the near-monodisperse NBS 705, Dow S-102, Dow S-109, and Dow S-111 were found to have either low or high molecular weight components in their molecular weight distributions. The characterization results on the Dow S-109 polystyrene fail, though, to explain the melt viscosity anomalies reported for this polymer.

INTRODUCTION

In a recent paper, Penwell and Graessley¹ discussed the differences in the zero-shear melt viscosities between the Dow S-109 polystyrene and other polystyrenes of comparable molecular weight. The Dow polystyrene had the lower viscosity—by a factor of about 2—and this difference was maintained over a temperature range of 141.8° to 227°C. The above authors¹ analyzed the Dow S-109 polystyrene via gel permeation chromatography (GPC) and, along with molecular weights from other sources, presented an $\langle M_w \rangle / \langle M_n \rangle$ of about 1.11 for this sample.

The viscosity discrepancy between the Dow S-109 and the other polystyrenes can most readily be explained by a peculiarity in the molecular weight distribution of the Dow S-109 polystyrene, i.e., a low molecular weight tail.¹ Hence, it was of interest to examine this polymer via GPC utilizing a seven-column set in order to maximize resolution. In the course of this investigation, other polystyrene standards were examined. These samples included the NBS 705, Dow S-102, Dow S-105, Dow S-108, and Dow S-111 polystyrenes.

EXPERIMENTAL

The Waters Ana-Prep instrument was used with seven 4-ft Styragel columns having porosities ranging from 2×10^3 to 5×10^6 Å. The experimental characteristics of this seven-column set have been reported elsewhere.² Tetrahydrofuran was the carrier solvent, and the detector was the Waters differential refractometer. Solution concentrations were 1/5% (wt/vol). Flow rates of 1/4 and

1 ml/min were used. Full-loop (2 ml) injections were made for both flow rates. A 5-ml syphon was used. Nineteen polystyrene standards were used to calibrate the seven-column set at the two flow rates. These polystyrenes included those from Waters Associates, Pressure Chemical, samples synthesized and characterized in these laboratories, and the polydisperse NBS-706 and Union Carbide SMD-3500. A linear calibration was obtained over the molecular weight range of 4×10^3 to 2.1×10^6 .

No corrections for dispersion or column broadening effects were made for the calculated GPC molecular weights determined in this work. McCrackin³ has shown that these corrections, for data from chromatograms obtained from the seven-column set used in this investigation, are unnecessary. At the 1 ml/min flow rate, McCrackin³ has calculated the P factor (which represents the resolving power for a column set) for these columns to be 0.98, while at the $\frac{1}{4}$ ml/min flow rate, the value of P is 0.99. For ideal resolution, P is equal to 1, while for real columns, P is less than 1. Hence, the molecular weight averages obtained by integrating the chromatograms should be corrected by P . However, for the columns, P is less than 1. Hence, the molecular weight averages obtained by integrating the chromatograms should be corrected by P . However, for the columns used in this work, the correction is only 1% and 2% for the flow rates of molecular weights reported herein. McCrackin's analysis and conclusions are fortified by the good agreement between the $\langle M_n \rangle$ and $\langle M_w \rangle$ values calculated from chromatograms generated by this seven-column set and those values determined from absolute measurements on a series of mono- and polydisperse polystyrenes.²

The NBS 705 and Dow polystyrenes were polymerized by *n*-butyllithium in benzene solution.⁴⁻⁷ Under the correct experimental conditions,⁸ this initiator will lead to the preparation of polystyrene possessing a near-monodisperse distribution of molecular weights for samples with molecular weights greater than 5×10^3 g/mole. These findings are in contrast with what is predicted from the initiation study of Bywater and Worsfold.⁹

Intrinsic viscosity measurements were made using a low-shear capillary viscometer. Benzene was used at a temperature of 25°C, while cyclohexane was used at 35°C.

RESULTS AND DISCUSSION

Figure 1 shows the gel permeation chromatograms of the Dow S-109 and NBS 705 polystyrenes obtained at the 1 and $\frac{1}{4}$ ml/min flow rates. It is readily apparent that these two polystyrenes possess virtually identical chromatograms. This conclusion is substantiated by a comparison of the chromatogram half-widths ($W/2$) and the molecular weights listed in Table I. No significant differences were found to exist between these two polystyrene samples.

Intrinsic viscosity measurements on the Dow S-109 polystyrene were made in benzene and cyclohexane. The values of $[\eta]$ determined were 0.74 ± 0.01 and 0.35 ± 0.01 dl/g, respectively, for each of the two solvents. These values are identical to those reported⁷ for the NBS 705 polystyrene. Both of the values reported here are based on three separate determinations in each of the two solvents.

Hence, there exists a strong indication that the Dow S-109 and NBS 705

TABLE I
Molecular Characteristics of the Dow S-109 and NBS 705 Polystyrenes Via Gel Permeation Chromatography^a

	Flow rate 1/4 ml/min				Flow rate 1 ml/min			
	$\langle M_n \rangle$ $\times 10^{-3}$ g/mole	$\langle M_w \rangle$ $\times 10^{-3}$ g/mole	$\langle M_w \rangle /$ $\langle M_n \rangle$	$W/2$ GPC counts	$\langle M_n \rangle$ $\times 10^{-3}$ g/mole	$\langle M_w \rangle$ $\times 10^{-3}$ g/mole	$\langle M_w \rangle /$ $\langle M_n \rangle$	$W/2$ GPC counts
Dow S-109	169	179	1.0 ₆	1.8 ₀	167	179	1.0 ₇	2.5 ₄
NBS-705	169	180	1.0 ₇	1.8 ₀	169	180	1.0 ₇	2.5 ₄

^a The molecular weights and chromatogram half-widths are based on four determinations for each sample of each flow rate. The standard deviation of the GPC (M_n) and (M_w) values in the measurements on the Dow S-109 and NBS 705 polystyrenes was not greater than 3%.

polystyrenes are the same sample. Both Stratten¹⁰ and Kratochvil¹¹ have indicated that this may be so. It is also interesting to note that Cazes¹² has recorded identical number- and weight-average molecular weights for these two polystyrene standards. It is also germane to note that the Dow Chemical Corp. was the source of the NBS 705 in 1961.^{7,13} Thus, this date is not in conflict with the date (1960) of the first published¹⁴ characterization data pertaining to the Dow

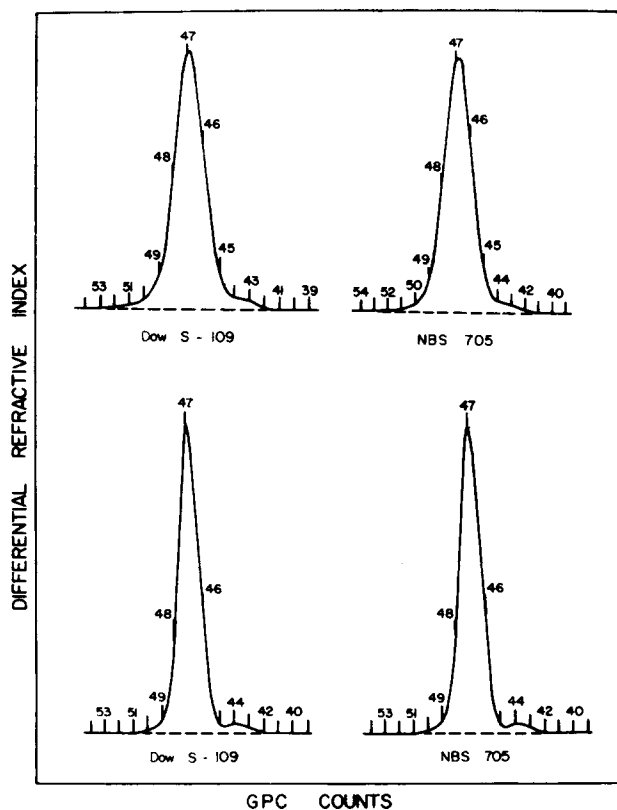


Fig. 1. Gel permeation chromatographs of Dow S-109 and NBS 705 polystyrenes: upper chromatograms, flow rate of 1 ml/min; lower chromatograms, flow rate of 1/4 ml/min.

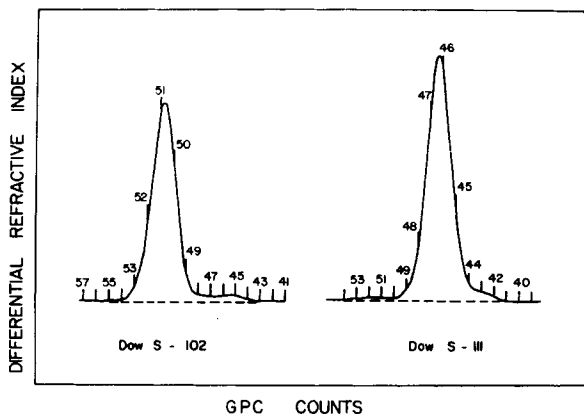


Fig. 2. Gel permeation chromatograms of Dow S-102 and Dow S-111 polystyrenes: flow rate of 1 ml/min.

S-109 polystyrene. However, the records which could resolve the question as to the identities of the Dow S-109 and NBS 705 polystyrenes are no longer extant.¹⁵ Boyer¹⁵ has indicated though, that no evidence exists from the synthesis standpoint that would vitiate the indication that these two polystyrenes are the same material.

The high molecular weight component (counts 42–45) seen in both the Dow S-109 and NBS 705 are identical and correspond to an $\langle M_n \rangle$ (GPC) of 3.3×10^5 g/mole and an $\langle M_w \rangle$ (GPC) of 3.5×10^5 g/mole. This higher molecular weight fraction represents nearly 4 wt-% of both the Dow S-109 and NBS 705 polystyrenes. Analysis of the NBS 705 via the ultracentrifuge has also revealed¹⁶ the presence of this high molecular weight moment in the molecular weight distribution.

This "dimer" of the parent material is probably the result of the presence of carbon dioxide or oxygen during the termination step. These species can cause the coupling¹⁷⁻¹⁹ of organolithium compounds.

It is of interest to note that recently published¹³ chromatograms of the NBS 705 polystyrene fail to show the high molecular weight fraction present in the chromatograms of Figure 1. This is doubtlessly due to the fact that too few columns were used in the analysis by the National Bureau of Standards.

Figure 2 contains the chromatograms of the Dow S-102 and Dow S-111 polystyrenes, while their molecular weights are presented in Table II. It can be seen that the Dow S-111 material contains a high molecular weight component (counts 41–44) similar to that seen in the Dow S-109 and NBS 705 standards. Unlike these samples, however, the Dow S-111 polymer contains a low molecular weight tail. The high molecular weight tail seen in the Dow S-102 sample cannot be accounted for via invoking a postpolymerization coupling reaction. Count 45, for example, on the chromatograph corresponds to a molecular weight of 2.6×10^5 g/mole. Nor can the presence of this high molecular weight fraction result from the linking reaction involving carbon dioxide, a reaction which leads to the formation¹⁷ of a three-armed "star" polystyrene. (A "star" polymer will always exhibit a longer residence time in the GPC columns than a linear material of the same molecular weight.) Thus, there does not appear to be a ready explanation for the presence of this high molecular weight fraction in the Dow S-102 poly-

TABLE II
Molecular Weights of NBS 705 and Dow Polystyrene Standards Via Gel Permeation Chromatography^a

Polystyrene	$\langle M_n \rangle \times 10^{-3}$, g/mole	$\langle M_w \rangle \times 10^{-3}$, g/mole	$\langle M_w \rangle / \langle M_n \rangle$	W/2 GPC counts
S-102 ^b	74	81	1.1 ₀	2.2 ₂
S-105	145	155	1.0 ₇	2.3 ₆
S-108	232	243	1.0 ₅	2.9 ₁
S-109	167	179	1.0 ₇	2.5 ₄
NBS-705	169	180	1.0 ₇	2.5 ₅
S-111	188	203	1.0 ₈	2.3 ₆

^a References 7 and 10 to 14 contain the molecular weights of these polystyrenes as determined via absolute methods. The values listed in this table are for the 1 ml/min flow rate. The sample listed in this table were synthesized by the late Dr. H. W. McCormick. Experimental errors: $\langle M_n \rangle \pm 4\%$, $\langle M_w \rangle \pm 4\%$. These error values are worst errors judged from GPC baseline uncertainties and other factors. The standard deviation of the GPC $\langle M_n \rangle$ and $\langle M_w \rangle$ values in measurements on the NBS 705 polystyrene was not greater than 3%.

^b The S-102 polystyrene has been reported²⁰ to possess an anomalously low (by 2.5 to 5°C) glass transition temperature when compared to a series of Pressure Chemicals near-monodisperse polystyrenes.

styrene other than to suggest that it may be a four-armed polystyrene "star." Although the formation of this species is potentially possible, the feasibility of this reaction remains to be demonstrated.

The remaining Dow polystyrene examined contained no evident abnormalities in their respective molecular weight distributions. The GPC molecular weights of the polystyrenes examined in this investigation are presented in Table II.

In conclusion, there exists convincing evidence that the Dow S-109 and the NBS 705 are the same sample. An additional fortifying point to be mentioned is that the melt viscosity value of the NBS 705 reported in reference 21 falls on the Dow S-109 viscosity-temperature plot compiled by Penwell and Graessley.¹

However, even though these two polystyrenes may be the same, this finding fails to clarify the melt viscosity differences reported by Penwell and Graessley.¹ A survey of the references reported in Table I of reference 1 reveals that only one sample²² (discounting the NBS 705 polystyrene) has been characterized with regard to *both* number- and weight-average molecular weights. The remaining four polystyrenes were characterized with regard to only viscosity or weight-average molecular weights.²³⁻²⁶ In this regard, it is appropriate to mention that at least three moments ($\langle M_n \rangle$, $\langle M_w \rangle$, and $\langle M_z \rangle$) are necessary to gain a quantitative description of the molecular weight distribution. Thus, in view of the apparent lack of any significant abnormality in the molecular weight distribution of the Dow S-109 polystyrene, the possibility exists that the anomalous viscosity behavior reported by Penwell and Graessley¹ may be due to the other polystyrenes presented in their comparison. Along this line, it is germane to note that a recent comparison of the melt viscosities of various anionically prepared polystyrenes has been made.²⁷ This comparison seemingly indicates that the Dow S-109 polystyrene lacks any anomalous behavior. However, this latter comparison,²⁷ unlike that of Penwell and Graessley,¹ was made at only one temperature.

It is thus evident that a resolution of this perplexing problem of the melt viscosity ambiguities awaits elucidation. It is also apparent that the answer to this problem will only be achieved when *well* characterized polystyrenes are analyzed. Toward this end, gel permeation chromatography can be the most revealing analytical tool available. However, this technique can yield inaccurate or incomplete information if too few columns are used or if the columns fail to cover the porosity range necessary to adequately resolve the molecular weight distribution of the sample. The results of this investigation and other work^{2,3,28,29} clearly demonstrate that gel permeation chromatography can yield detailed and accurate insight into the molecular weight distributions of both polydisperse and near-monodisperse polymers. It has been shown³ and indicated^{2,28,29} that corrections for column broadening effects on molecular weights are unnecessary if an adequate number of columns are used in the analysis.

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References

1. R. C. Penwell and W. W. Graessley, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 213 (1974).
2. L. J. Fetters and M. Morton, *Macromolecules*, **7**, 512 (1974).
3. F. L. McCrackin, *J. Appl. Polym. Sci.*, **21**, no. 1, (1977).
4. H. W. McCormick, *J. Polym. Sci.*, **36**, 341 (1959).
5. H. W. McCormick, F. M. Bower, and L. Kin, *J. Polym. Sci.*, **39**, 87 (1959).
6. D. McIntyre, *J. Res. Nat. Bur. Stand.*, **71A**, 43 (1967).
7. National Bureau of Standards Certificate, Standard Sample 705, Polystyrene.
8. M. Morton and L. J. Fetters, *Rubber Rev.*, **48**, 359 (1975).
9. S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **38**, 1891 (1960).
10. R. A. Stratton, *J. Colloid Interfac. Sci.*, **22**, 517 (1966).
11. J. P. Kratochvil, in *Characterization of Macromolecular Structure*, D. McIntyre, Ed., Publication 1573, National Academy of Sciences, Washington, D.C., 1968, p. 59.
12. J. Cazes, *J. Chem. Educ.*, **43**, A625 (1966).
13. H. L. Wagner, National Bureau of Standards Special Publication 260-33, Washington, D.C., 1972.
14. J. F. Rudd, *J. Polym. Sci.*, **44**, 459 (1960).
15. R. F. Boyer, private communication, May 7, 1975.
16. D. McIntyre, unpublished data.
17. D. P. Wyman, V. R. Allen, and T. Altares, Jr., *J. Polym. Sci. A*, **2**, 4545 (1964).
18. H. Yasuda, M. Walczak, W. Rhine, and G. Stucky, *J. Organomet. Chem.*, **90**, 123 (1975).
19. E. M. Firer, Ph.D. Thesis, The University of Akron, 1973.
20. A. Rudin and B. Burgin, *Polymer*, **16**, 291 (1975).
21. J. Pannell, *Polymer*, **12**, 547 (1971).
22. D. J. Plazek and V. M. O'Rourke, *J. Polym. Sci. A-2*, **9**, 209 (1971).
23. T. G. Fox and P. J. Flory, *J. Amer. Chem. Soc.*, **70**, 2384 (1948).
24. S. Onogi, H. Kato, S. Ueki, and T. Ibaragi, *J. Polym. Sci. C*, **No. 15**, 481 (1966).
25. R. L. Ballman and R. H. M. Simon, *J. Polym. Sci. A*, **2**, 3557 (1964).
26. R. Suzuki, Ph.D. Thesis, Faculté des Sciences de Strasbourg, 1970.
27. A. Casale, R. S. Porter, and J. F. Johnson, *Rev. Macromol. Chem.*, **6**, 387 (1971); *J. Macromol. Sci.-Rev. Macromol. Chem.*, **C5**, 387 (1971).
28. M. Ambler, L. J. Fetters, and Y. Kesten, *J. Appl. Polym. Sci.*, **21**, (1977).
29. Roestamsjah, L. A. Wall, R. E. Florin, M. H. Aldridge, and L. J. Fetters, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1783 (1975).

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