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Standard Reference Materials:

COMPARISON OF ORIGINAL AND SUPPLEMENTAL SRM 705, NARROW MOLECULAR WEIGHT DISTRIBUTION POLYSTYRENE

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Standard Reference Materials:

Comparison of Original and Supplemental SRM 705, Narrow Molecular Weight Distribution Polystyrene

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Washington, D.C. 20234

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Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth will receive prompt attention from:

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COMPARISON OF ORIGINAL AND SUPPLEMENTAL SRM 705, NARROW MOLECULAR WEIGHT DISTRIBUTION POLYSTYRENE

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Because the supply of the original batch of narrow molecular weight distribution polystyrene, SRM 705, is almost exhausted, another supply of polystyrene, reported to be from the same batch as the original has been characterized to determine whether it is the same as the original as far as the properties listed on the certificate are concerned. No difference in molecular weight as measured by light-scattering, osmometry, or gel-permeation chromatography could be found. The limiting viscosity numbers were also the same. It was also shown from solution viscosity measurements that pellet to pellet variation in molecular weight is negligible.

Key words: Characterized polymers; narrow molecular weight polystyrene; polystyrene standard; Standard Reference Material 705.

1. INTRODUCTION

Early in 1963 the National Bureau of Standards issued its first polymer Standard Reference Material, SRM 705 [1], a narrow molecular weight distribution polystyrene. Recently the original supply of one of these, SRM 705, became very low, but additional material, which had previously been sent to the Bureau by Dow Chemical Company, was available. According to the letter by Dr. H. W. McCormick of Dow Chemical Company, Midland, Michigan, dated September 7, 1966, to Dr. Emanuel Horowitz, this additional supply is the same as the original. Because this is a certified material, however, it was necessary to compare the original and the new material to make certain that the two are indistinguishable as far as the properties listed on the certificate are concerned. About 4900 grams of this second sample are available and will be referred to as SRM 705A in this report only.

This polystyrene, produced by Dr. McCormick's group at Dow Chemical Company by large scale anionic techniques, has a very narrow molecular weight distribution--M_w/M_n of about 1.12. It had been certified previously by Dr. D. McIntyre and his group at the National Bureau of Standards for weight average molecular weight by light scattering and sedimentation equilibrium, number average molecular weight by membrane osmometry, and limiting viscosity number in benzene and cyclohexane. A copy of the certificate is shown in Appendix 1.

In the present study SRM 705 and 705A were compared for weight average molecular weight, for number average molecular weight and for limiting viscosity number. In addition they were compared for molecular weight distribution by gel permeation chromatography, a technique which was not available at the time the SRM 705 was originally issued. No comparison was made in this work using the ultracentrifuge.

In the discussion which follows no attempt is made to describe equipment or techniques where this has already been done satisfactorily elsewhere. However, when changes were made in the standard procedure, or when there is no common standard procedure, details of the method are given.

2. WEIGHT AVERAGE MOLECULAR WEIGHT BY LIGHT SCATTERING

A comparison of the weight average molecular weight of SRM 705 and SRM 705A was made using the "Sofica" photo-gonio diffusometer, Model 701 (Bausch and Lomb, Rochester, New York).* A general description of the light scattering

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* Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

method may be found in several places, as for example in the chapter by Chiang [2]. For a description of the specific techniques used in this laboratory, the paper on light scattering in the series [3] describing the certification of SRM 1475, linear polyethylene, is recommended. Determinations were carried out in cyclohexane, at the theta temperature, 35 °C, with unpolarized light at 5460Å. It was generally found that less scatter was obtained in the data by placing an additional 5460Å light filter just before the detector photocell. It is possible that this filter removed extraneous radiation due to fluorescence in the polymer solution.

The instrument was calibrated with benzene, for which the Rayleigh ratio is taken as $15.8\text{x}10^{-6}\text{cm}^{-1}$ [4]. In practice, a special glass rod is used as a working standard, after comparison of its scattering with the pure benzene.

Six different concentrations, ranging from about $1\text{x}10^{-3}$g/ml to $5\text{x}10^{-3}$g/ml of each polymer were measured. Each solution was made up independently by weight and then filtered through "Millipore" filters of 0.22 μm, nominal pore size, to remove dust and other particulate matter which might interfere with scattering at low angles. The solutions were kept at 40 °C until measured at 35 °C. Replicate measurements were made on two different samples of each solution.

The value of the refractive index increment, dn/dc for the polystryrene-cyclohexane system at 35 °C was taken as 0.1705 ml/g [5].

The value of c/I for each concentration was plotted against $\sin^2\theta/_2$ and extrapolated visually to $\theta = 0$. All these extrapolated c/I's were then plotted against concentration and again extrapolated to $c = 0$. A similar procedure was followed for these values of c/I, at each specified angle, as a function of concentration. The values of c/I extrapolated to $c = 0$ for each angle were then plotted against $\sin^2\theta/_2$ to find the value of c/I at $\theta = 0$. The mean of this value and the value obtained at $c = 0$, which almost always were within 1/2% of each other, was used to obtain 1/M upon multiplication by the appropriate factor. The results follow:

Table 1. Direct Comparison of 705-705A by Light Scattering.

	M_w	
Sample 705:	182,300	
	183,900	
		Average 183,100
705A:	183,000	
	184,100	
		Average 183,550
Certificate value:	179,300	

It was possible, because of the availability of some subsequent determinations on 705, made in another connection, to obtain a better value for the mean and standard deviation. These additional determinations gave the following values:

Table 2. Additional Determinations of M_w on 705.

	183,000
	177,500
	180,900
	182,700
	177,100
Mean	180,240

As shown in Table 3, the difference between the mean for the first set, (Table 1) and the above is 2860, well within the 95% confidence limits of the difference. Hence we may assume that the two sets of data may be treated as one set.

If we compare the mean of this combined set, 181,111, with the mean for 705A, 183,550 (Table 1) we find that the difference, 2539, between the two is also within the 95% confidence limits value, 4,900. This is also shown in Table 3. Hence there is no evidence of a difference between the two materials.

We also conclude that there is no difference between the value on the certificate and the value now obtained for 705, again as seen in Table 3. It should be noted that since there is no reason to believe that the standard

Table 3. Comparison of M_w for 705 - 705a

		705 (Table 1)	705 (Table 2)	705 (Tables 1 & 2)	705a	705 (Tables 1 & 2)	Certificate Value
Number of measurements		2	5	7	2	7	9
Mean		183,100	180,240	181,111	183,550	181,111	179,300
Standard deviation	s	1131	2805	2756	778	2756	2220
Difference	d	2860		2439		1811	
Total degrees of freedom	ϕ	5		7		11.4(2)	
Pooled standard deviation		2559		2568		-	
Estimated standard error of the difference	s_d	2141		2059		1278	
	$t^{(1)}$	2.57		2.36		2.18	
Difference	$d \pm ts_d$	2860 ± 5502		2439 ± 4859		1811 ± 2786	

(1) Probability points of the t distribution

(2) Where standard deviations are not necessarily equal, total degrees of freedom, ϕ, when comparing two means 1 and 2 is [6]

$$\frac{1}{\phi} = \frac{1}{\phi_1}\left[\frac{s_1^2\ n_1}{s_1^2/n_1 + s_2^2/n_2}\right]^2 + \frac{1}{\phi_2}\left[\frac{s_2^2/n_2}{s_1^2/n_1 + s_2^2/n_2}\right]^2$$

where n is the number of observations

deviations of the present set of measurements and of the certificate value are equal, the standard deviations were not pooled. In addition, the number of degrees of freedom was estimated by the method shown in the footnotes to Table 3.

In other cases shown in Table 3 the standard deviations were pooled.

3. NUMBER AVERAGE MOLECULAR WEIGHT BY OSMOMETRY

Number average molecular weight was determined by osmotic pressure measurements. Techniques for determining the number average molecular weight by osmotic pressure are described in the literature [7, 8]. The details of the method used in this laboratory are included in the paper on osmometry describing the certification of SRM 1475 [9]. These were made with a Hewlett-Packard Membrane Osmometer, Model 502, which is characterized by rapid response time (a few minutes), negligible solvent transfer across the membrane, and small sample volume (0.3 ml). The semipermeable membranes were gel cellophane, type 450 D, obtained from Arro Laboratories, Inc. These, when received, are in an isopropanol-water solution. They are then conditioned by soaking successively in ethanol, 1:1 ethanol-acetone, 1:1 acetone-toluene, and finally pure toluene, the solvent used for the measurements.

When the osmotic pressure measurements were begun, it was not known that the pellet-to-pellet variability was negligible, as shown by the viscosity measurements described below. To eliminate the effects of possible pellet-to-pellet variability and to bring both materials to the same physical condition, particularly moisture content, the following procedure was utilized.

Five replicate one-gram blends of pellets of 705 and 705A were separately dissolved in benzene and freeze dried. From each of these ten samples, five independent concentrations, ranging from 0.25 g/100 ml to about 1.1 g/100 ml were made up in toluene to give a total of 50 solutions. The osmotic pressure, Π, of each of these was measured twice at 25 °C.

The limiting values of Π/c as the concentration, c, approaches zero were determined for each of these ten solutions in three ways.

1. linear least squares Π/c vs c
2. linear least squares $(\Pi/c)^{1/2}$ vs c
3. least squares - polynomial $\Pi = d_1c+d_2c^2+d_3c^3$

Method 3, which is perhaps the most desirable of the above methods for treating the data, gave, with our computer program, at least one result that was extremely sensitive to one point that was just off a smooth curve. Further investigation is needed before a satisfactory method of fitting such data to a polynomial is found. For our immediate needs, it was sufficient to compare the results for the two polymers obtained by method 2 above, i.e., plotting $(\Pi/c)^{1/2}$ vs c and determining the limiting value of $(\Pi/c)^{1/2}$ from the intercept at c = 0 by a linear least squares computation. This limiting value is inversely proportional to the square root of the molecular weight. The results are shown in Table 4, where $(\Pi/c)_o$ represents the square of this limiting value.

To determine whether the difference between the averages of M_n for the two--162,400 for 705 and 165,200 for 705A--is significant, the same procedure was employed as in the light scattering case. A combined standard error of 3,500 is found for the two sets of data, and since this, when multiplied by a t value of 2.31 for 8 degrees of freedom, gives, for 95% confidence limits, a value of 8,000, we conclude that the difference of the two number average means of 2,800 is not significant.

If the 705A value is compared with the certificate value of 170,900, determined in cyclohexane at 35 °C with a standard deviation of the average 580 (number of determinations was 12), the estimated standard error of the difference is 2,960 with 4 degrees of freedom, calculated as shown in Table 3. The t value is 2.78 which when multiplied by the combined standard error above gives a 95% confidence limit of 8,200, indicating that the difference of 5,680 molecular weight units is not significant.

The standard error of 580 in the certificate is surprisingly low but since the details of this determination

Table 4. Number Average Molecular Weight $(\Pi/c)^{1/2}$ Method

705				705a			
Sample Number	$(\Pi/c)_o$ cm-liter/g	Standard Deviation of $(\Pi/c)_o$	M_n	Sample Number	$(\Pi/c)_o$ cm-liter/g	Standard Deviation of $(\Pi/c)_o$	M_n
I	0.1887	0.00285	160,670	Ia	0.1834	0.00922	165,310
II	.1861	.00283	162,910	IIa	.1835	.00150	165,220
III	.1802	.00126	168,250	IIIa	.1925	.00232	157,500
IV	.1934	.00431	156,760	IVa	.1729	.00315	175,350
V	.1853	.00514	163,620	Va	.1836	.00263	162,740
Average			162,440				165,220

Statistical Data:

Difference in M_n:	2,780	
Pooled standard deviation, s	5,467	
Estimated standard error of the difference (S.E.)	3,458	
t (8 degrees of freedom)	2.31	
Confidence limits, 95% (txS.E.)		7,987
Difference between 705 and 705a	2,780 ±	7,987

Certificate Data: M_n: 170,900

Standard deviation of the average: 580
Number of determinations: 12

are not available, it is difficult to make a comparison with our experiments.

4. LIMITING VISCOSITY NUMBERS

Limiting viscosity number, L.V.N., was determined in the usual way by extrapolation, to zero concentration, of viscosity number $(\eta/\eta_o - 1)/c$, where η/η_o is the relative viscosity of solution to solvent, and c is the concentration in g/ml. The measurements were made in a Ubbelohde viscometer. A Hewlett-Packard, Model 5901B Autoviscometer, was used to operate the viscometer and measure the flow times, while the viscometer was thermostatted in a Hewlett-Packard 5901A Constant Temperature Bath. With this system, flow times of about 40 or 50 seconds for a given solution are reproducible to about 0.03 seconds, making it possible to use fairly dilute solutions and thereby increasing the reliability of the extrapolation to zero concentration. Six solutions of each sample in distilled cyclohexane, ranging in concentration from .004 g/ml to 0.1 g/ml were measured at 35 °C. As in the case for light scattering, the solutions were kept at 40 °C until used. The results were:

Table 5. Limiting Viscosity Number in Cyclohexane at 35 °C.

	L.V.N.	Standard Deviation
705	35.2 ml/g	0.2
705A	35.3	0.1
Certificate value	35.4	0.24*

* "Standard deviation of average, for six samples".

Again there is no evidence for a difference between 705 and 705A, nor between their average and the certificate value.

5. GEL PERMEATION CHROMATOGRAPHY MEASUREMENTS

The two samples were compared by gel permeation chromatography, a column fractionation method that has come into general use in recent years for the determination of molecular weight distribution of high polymers.

The gel permeation chromatograph used was the Model 200 (analytical scale) G.P.C. manufactured by Waters Associates, 61 Fountain Street, Framingham, Massachusetts. It was run at 100 °C with 1,2,4-trichlorobenzene as the solvent, at a concentration of 0.3%.

Since only the difference between 705 and 705A was of interest, an absolute, carefully determined independent calibration was not required. Instead two anionically produced polystyrenes, supplied by Waters Associates, with molecular weight falling on either side of the SRM 705 value (41,000 and 98,000) and the SRM 705 (certificate value M_w = 179,300) were run to give the following calibration:

$$\log M = 11.89 - 0.204\ V_e$$

where V_e is the peak elution volume.

Visual comparison of the charts (figure 1) for runs made under the same conditions for 705 and 705A show that the peaks occur at the same elution volume. Calculation of the number, weight and z average molecular weights, given

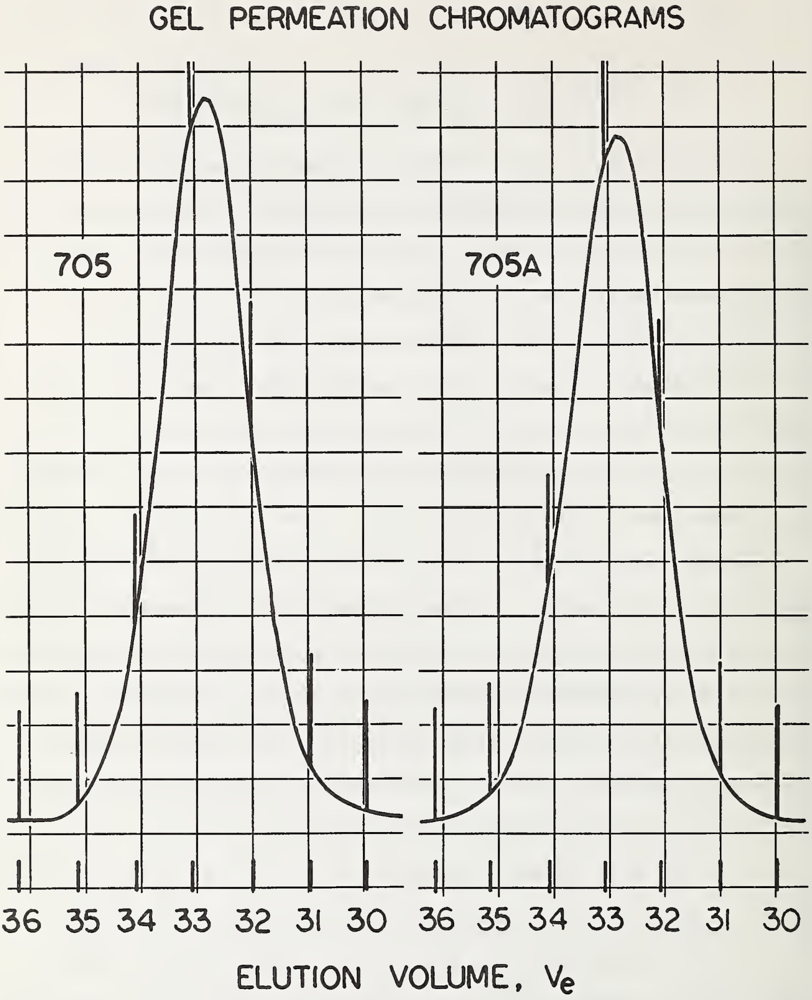


Figure 1. Comparison of gel permeation chromatograms of 705 and 705A.

in Table 6, show that no significant differences in distribution occur. If the curves in figure 1 were normalized, they would be superimposable.

Table 6. G. P. C. Data.

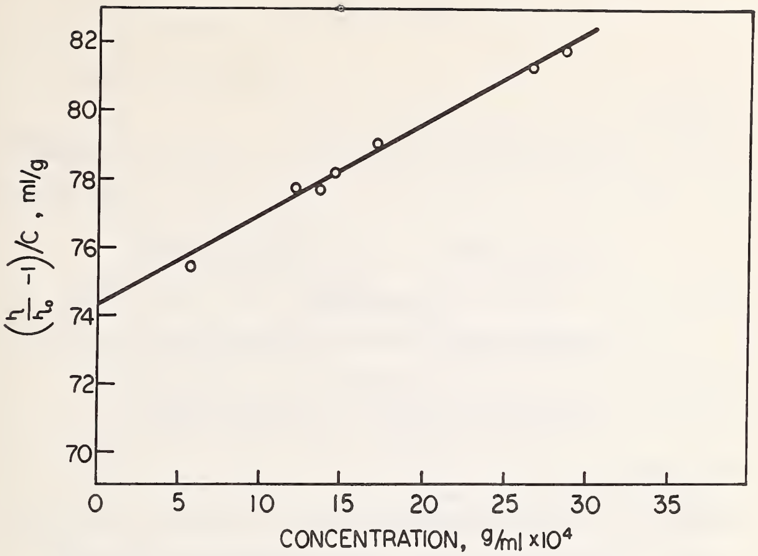
	Run	M_n	M_w	M_z
705	1	155,600	178,200	206,000
	2	155,900	177,900	204,000
705A	1	157,000	180,200	208,000
	2	157,800	181,500	211,000

The replication is insufficient to provide a good measure of the reproducibility among solutions. However, the difference in molecular weights found between 705 and 705A is of the order of about 2%, which we know from previous experience to be statistically insignificant, so we again conclude that there is no evidence of an important difference between the two materials.

Because of the method of calibration, the molecular weights quoted above should not be considered absolute.

6. DETERMINATION OF PELLET TO PELLET VARIATION

Since the polymer pellets weigh only between 7 to 20 mg, there are only two techniques available to us which take a small enough sample size, namely G. P. C. and solution viscosity, with which to obtain a measure of variation in molecular weight from pellet to pellet. Since in our case viscosity measurements are more sensitive to small changes in molecular weight than G. P. C., the former was used. It was possible to obtain meaningful results with a "semimicro" Cannon-Ubbelohde viscometer which takes a one milliliter sample. Single pellets were dissolved in 5 to 10 ml of benzene and measured at 35 °C. Because of variation in pellet weight, it was not convenient to keep the concentration constant, so that the following procedure was used to estimate the variation in viscosity. The viscosity number $(\eta/\eta_0-1)/c$ for each pellet is computed from flow times of solvent and solution, corrected for kinetic energy effects, and is plotted against concentration. These are shown in figure 2, together with the line representing the linear least squares fit of the points. The standard deviation of the points about the line is about 0.3% of the value of the intercept on the viscosity number axis, or the limiting viscosity number. This represents the sum of measurement error and pellet to pellet variation in viscosity or molecular weight. From previous measurements it has been established that measurement error itself leads to a standard deviation of 0.3%, leading to the conclusion that the variation in viscosity, and hence molecular weight, from pellet to pellet, is negligible.



7. SUMMARY

No evidence of a difference between 705 and 705A can be shown to exist. From solution viscosity measurements it was shown that pellet to pellet variation in molecular weight is negligible.

The author acknowledges the assistance of J. E. Brown, R. G. Christensen, and J. R. Maurey who carefully performed the measurements discussed in this report. He is also grateful to Dr. John Mandel for helpful discussion of the statistical analyses employed.

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APPENDIX I.

U. S. Department of Commerce
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Standard Reference Material 705

Polystyrene

(Narrow Molecular Weight Distribution)

Donald McIntyre

	Number of Determinations	Average	Standard Deviation of Average
Number-Average Molecular Weight (Measured by osmotic pressure)	12	170,900**	580
Weight-Average Molecular Weight (Measured by light scattering)	9	179,300*	740
Weight-Average Molecular Weight (Measured by sedimentation equilibrium)	22	189,800*	2,100
Limiting Viscosity Number (ml/g) (Intrinsic viscosity)			
Benzene, 25 °C	5	74.3*	0.18
Benzene, 35 °C	13	74.5***	0.23
Cyclohexane, 35 °C	6	35.4*	0.24
Ratios of Molecular Weight (Based on fractionation)		$M_z:M_w:M_n$ = 1.12:1.07:1	

*Average of individual determinations made on a pooled sample combining portions of material taken from the entire lot.

**The average includes results from the pooled sample and from a separate study made to determine possible heterogeneity of the lot. It was found that samples taken from different locations showed slightly more variability than samples taken from adjacent locations. The standard deviation of the reported average includes the effect of lot heterogeneity.

***The average is obtained from a study made on samples from six locations to determine possible heterogeneity

(over)

of the lot. It was found that samples taken from different locations showed slightly more variability than samples taken from adjacent locations. The standard deviation of the reported average includes the effect of lot heterogeneity.

Washington, D. C. 20234 J. Paul Cali, Chief
November 6, 1969 Office of Standard Reference Materials
(Revised February 25, 1972)

The polystyrene sample was prepared by the polymerization of styrene in benzene using butyllithium as an initiator. Ash content is 0.05% of sample. Volatile content is about 0.5%. Determinations of molecular weight and intrinsic viscosity are based on sample weights of the polystyrene pellets uncorrected for volatiles. Each pellet weighs approximately 10 mg. Several pellets were always used in the above determinations.

The osmotic pressure measurements were made with #600 gel cellophane membranes. The light scattering and sedimentation molecular weight determinations were calculated using the following constants for polystyrene-cyclohexane solutions at 35 °C: 0.1705 ml/g for the refractive index increment at 546 nm and 0.930 ml/g for the partial specific volume. The maximum rate of shear in the Ubbelohde viscometers used to determine the intrinsic viscosities was about 1500 $\sec^{-1}$ for water. The z-average (M_z), weight-average (M_w), and number-average (M_n), molecular weight ratios are based upon a complete viscometric analysis and selected osmometric analysis of 36 fractions.

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Herman L. Wagner

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15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Becuase the supply of the original batch of narrow molecular weight distribution polystyrene, SRM 705, is almost exhausted, another supply of polystyrene, reported to be from the same batch as the original has been characterized to determine whether it is the same as the original as far as the properties listed on the certificate are concerned. No difference in molecular weight as measured by light scattering, osmometry, or gel-permeation chromatography could be found. The limiting viscosity numbers were also the same. It was also shown from solution viscosity measurements that pellet to pellet variation in molecular weight is negligible.

17. KEY WORDS (Alphabetical order, separated by semicolons) Characterized polymers; narrow molecular weight polystyrene; polystyrene standard; Standard Reference Material 705.

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