National Institute of Standards & Technology

Certificate

Standard Reference Material 1475a

Linear Polyethylene

(Whole Polymer)

This Standard Reference Material (SRM) is intended for the calibration and evaluation of instruments used in polymer technology and science for the determination of molecular weight and molecular weight distribution and for use as a characterized sample for measurements of other physical properties of linear polyethylene. This SRM is supplied as pellets of polyethylene in a 50 g unit.

Property	Certified Value*		
Melt-Flow Rate[a], g/10 min	2.02	±	0.24[a]
Molecular Weights, g/mol:			
Weight-average molecular weight[b]	52,000	±	2,000
Number-average molecular weight[c]	18,310	±	360
Weight-average molecular weight[c]	53,070	±	620
Z-average molecular weight[c]	138,000	±	3,700
Ratio of molecular weight M_z:M_w:M_n[c]	7.54:2.90:1		
Molecular weight distribution[c]	(See Table 1)		
Limiting Viscosity Numbers[d], mL/g:			
at 130 °C in 1-chloronaphthalene	89.0	±	0.32
at 130 °C in 1,2,4-trichlorobenzene	101.0	±	0.86
at 130 °C in decahydronaphthalene[e]	118.0	±	0.32
Solid Density[f], g/cm^3	0.97844	±	0.00004
Heat Capacity	(See Table 2)		

*Melt-Flow Rate uncertainty parameters are described in Table 3. All other uncertainties are expressed as the standard deviation of the mean.

[a]By procedure A, ASTM Method D1238-90b, Test Condition 190/0.325.
[b]By light scattering in 1-chloronaphthalene at 135 °C.
[c]By size exclusion chromatography.
[d]Sample must be of adequate size. See directions for use on page 3.
[e]"Technical" grade, which assayed at approximately equal proportions of cis- and trans-decahydronapthalenes.
[f]By ASTM Method D1505-67; sample prepared by procedure A, ASTM Method D1928-68.

Gaithersburg, MD 20899
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(Revision of certificate dated 7-1-93)

Thomas E. Gills, Acting Chief
Standard Reference Materials Program

(over)

Original certification of SRM 1475 was performed in the NIST Polymers Division by C.A.J. Hoeve, H.L. Wagner, J.E. Brown, A.B. Bestul, S.S. Chang, R.G. Christensen, L.J. Frolen, J.R. Maurey, G.S. Ross, and P.H. Verdier. Measurements comparing SRM 1475a to SRM 1475 were performed by C.M. Guttman and J.R. Maurey of the NIST Polymers Division.

The technical and support aspects involved in the revision, update, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.C. Colbert.

NOTICE AND WARNING TO USERS

Expiration of Certification: This certification is valid for five years from date of shipment from NIST.

Storage: SRM 1475a should be stored in its original bottle, tightly closed, and under normal laboratory conditions.

Table 1. Cumulative Molecular Weight Distribution by Gel-Permeation Chromatography

Log M	Wt %	Log M	Wt %	Log M	Wt %
2.800	0.0	4.014	15.2	5.065	90.7
2.865	0.005	4.070	18.1	5.113	92.2
2.929	0.020	4.126	21.5	5.161	93.7
2.992	0.052	4.182	25.2	5.209	94.8
3.056	0.105	4.237	29.3	5.256	95.8
3.119	0.185	4.292	33.7	5.303	96.6
3.181	0.343	4.346	38.5	5.349	97.3
3.243	0.475	4.400	43.4	5.395	97.9
3.305	0.706	4.454	48.5	5.440	98.4
3.366	0.999	4.507	53.5	5.485	98.7
3.427	1.38	4.560	58.3	5.530	99.1
3.488	1.88	4.612	62.9	5.574	99.3
3.548	2.51	4.664	67.3	5.618	99.5
3.607	3.30	4.715	71.4	5.662	99.7
3.667	4.28	4.766	75.1	5.705	99.8
3.725	5.46	4.817	78.5	5.789	99.9
3.784	6.87	4.868	81.6	5.87	100.0
3.842	8.56	4.918	84.4		
3.900	10.50	4.967	86.7		
3.957	12.7	5.016	88.9		

MATERIAL SOURCE AND PREPARATION

This sample of linear polyethylene was obtained from E.I. duPont de Nemours and Company of Wilmington, DE. It has an ash content of 0.002%. No volatiles were detected by a gas-chromatographic procedure capable of detecting 0.5% volatiles. The manufacturer added 111 mg/kg of the antioxidant, Irganox 1010 (Ciba-Geigy), which is tetrakis [methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate] methane.

The size exclusion chromatograph was calibrated with linear polyethylene fractions obtained by a column elution technique. These fractions were characterized for use in the calibration procedure by determining their weight-average molecular weights by light-scattering, and their number-average molecular weights by membrane osmometry.

Directions for Use: A pellet-to-pellet coefficient of variation of 3% in the limiting viscosity number was found. All determinations should be performed on samples containing at least 50 pellets or 1 g of polymer (or material from a 1 g homogeneous blend). This will reduce the expectation of the standard error due to pellet variability to less than 0.5%.

For determination of melt flow rate by automated procedure B in the ASTM Method, the melt density can be found in Table 4 of ASTM D1238-90b.

Heat Capacity: Heat capacities C_p (ρ,T) at various temperatures are given at two 23 °C densities, ρ = 0.954 and ρ=1.000 g/cm^3 in Table 2. These density values differ from the certified density value in this certificate. [2,3]

At densities between 0.954 and 1.000 g/cm^3, obtained by varying the thermal history and crystallization conditions, the heat capacity is given by:

$$C_p(\rho,T) = C_p\ (1.000,\ T) + \frac{1-\rho}{0.17\rho}\ \Delta C(T),$$

where $\Delta C(T)$ is also tabulated in Table 2. These values may be used to check the values obtained with dynamic thermal analysis instruments when the heating rate approaches zero.

Errors in calculated $C_p(\rho,T)$ are believed to be less than 1% between 25 and 360 K and increase to about 5% at 5 K.

Table 2. Heat Capacity per Mole (14.027 g) of [-CH_2-]

T K	C_p(0.954,T)	C_p(1.000,T)	ΔC(T)
	----------J/(mol•K)----------		
5	0.024	0.014	0.038
10	0.173	0.106	0.235
15	0.473	0.342	0.458
20	0.904	0.727	0.619
25	1.433	1.231	0.706
30	2.027	1.819	0.728
35	2.664	2.465	0.702
40	3.322	3.135	0.652
45	3.981	3.811	0.587
50	4.626	4.475	0.516
60	5.841	5.730	0.385
70	6.935	6.855	0.288
80	7.911	7.847	0.230
90	8.786	8.725	0.208
100	9.579	9.511	0.226
110	10.31	10.23	0.30
120	11.01	10.88	0.47
130	11.70	11.49	0.78
140	12.44	12.07	1.31
150	13.18	12.62	1.98
160	13.91	13.17	2.61
170	14.61	13.73	3.15
180	15.30	14.30	3.59
190	15.98	14.87	3.94
200	16.66	15.47	4.25
210	17.36	16.08	4.58
220	18.10	16.70	5.00
230	18.91	17.35	5.55
240	19.80	18.03	6.29
250	20.76	18.72	7.22
260	21.76	19.45	8.19
270	22.78	20.23	9.06
280	23.80	21.04	9.81
290	24.83	21.89	10.47
300	25.87	22.76	11.09
310	26.95	23.64	11.80
320	28.11	24.54	12.72
330	29.39	25.46	13.97
340	30.86	26.46	15.63
350	32.59	27.57	17.76
360	34.65	28.90	20.31
273.15	23.10	20.48	9.31
298.15	25.68	22.60	10.93

Table 3

Estimates of Uncertainties in Melt Flow Rate of SRM 1475a
Polyethylene Under Condition 190/0.325 [4,5]

1.	Uncertainty due to repeatability of experiment	0.36%
2.	Uncertainty due to instrument variability as estimated from reproducibility reported in ASTM method	11%
3.	Uncertainty due to mass measurement	0.0%
4.	Uncertainty due to time interval measurement	0.0%
5.	Uncertainty due to melt temperature measurement	0.7%
6.	Combined expanded uncertainty, U_c[a]	12%

a. The combined expanded uncertainty computed by root-sum-of-squares of the component uncertainties was only 11.03%, not statistically distinguishable from the component uncertainty due to reproducibility alone, 11%, considering the uncertainty in reproducibility itself. The combined expanded uncertainty is rounded up to U_c=12%.

SUPPLEMENTAL INFORMATION

The methyl [-CH_3] group content as determined by ASTM Method D2238-68 is 0.15 methyl groups per 100 carbon atoms. This shows the polyethylene to be essentially linear. The differential refractive index in 1-chloronaphthalene, required for the calculation of molecular weight by light scattering, was found to be -0.193 mL/g at 135 °C and 546 nm. The maximum rate of shear in the Ubbelohde viscometer was about 1500 s^{-1}. All measurements were carried out at specific viscosities (0.1 or less) which were sufficiently low for negligible dependence on rate of shear.

Reports describing investigations required for the certification of SRM 1475 (previous lot) are described in references 1-3. A report describing the investigations comparing this current lot, SRM 1475a, with SRM 1475 can be found in reference 4.

REFERENCES

[1] Hoeve, C.A.J., et al., J. Res. NBS, 76A, 137-170, (1972).

[2] Chang, S.S., and Bestul, A.B., J. Res. NBS, 77A, 395-405, (1973).

[3] Chang, S.S., J. Res. NBS, 78A, 387-400, (1974).

[4] Guttman, C.M. and Maurey, J.R., "Recertification of the SRM 1975a, A Linear Polyethylene Resin," NISTIR 5199, (1993).

[5] Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Tech. Note 1297, (Jan. 1993).