U.S. Department of Commerce
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National Bureau of Standards
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National Bureau of Standards Certificate

Standard Reference Material 1475

Linear Polyethylene

(Whole Polymer)

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This Standard Reference Material is intended for the calibration of instruments used in polymer science and technology for the determination of molecular weight and molecular weight distribution and for use in checking dynamic thermal analytical instruments.

Property	Value	Standard deviation of the mean
Molecular Weights, g/mol:		
Weight-average molecular weight[a]	52,000	2,000
Number-average molecular weight[b]	18,310	360
Weight-average molecular weight[b]	53,070	620
Z-average molecular weight[b]	138,000	3,700
Ratio of molecular weights M_z:M_w:M_n[b]	7.54:2.90:1	
Molecular weight distribution[b]	See Table 1	
Limiting Viscosity Numbers,[c] mL/g:		
at 130 °C in 1-chloronaphthalene	89.0	0.32
at 130 °C in 1,2,4-trichlorobenzene	101.0	.86
at 130 °C in decahydronaphthalene[d]	118.0	.32
Melt-Flow Rate,[e] g/10 min	2.07	.0062
Density,[f] g/cm^3	0.97844	.00004
Heat Capacity	See Table 2	

[a] By light scattering in 1-chloronaphthalene at 135 °C.
[b] By gel-permeation chromatography.
[c] Sample must be of adequate size. See notes at the end of this certificate.
[d] "Technical" grade, which assayed at approximately equal proportions of cis- and trans- decahydronaphthalenes.
[e] By a procedure similar to Procedure A, ASTM Method D1238-65T, Test Condition D, 190 °C, load 325 g.
[f] By ASTM Method D1505-67; sample prepared by Procedure A, ASTM Method D1928-68.

The support aspects involved in the issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. W. Mears and R. K. Kirby.

Washington, D.C. 20234
December 8, 1978
(Revision of certificates
dated 11-6-69 & 12-2-71)

J. Paul Cali, Chief
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(over)

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		

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

The methyl 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. A pellet-to-pellet coefficient of variation of 3 percent in the limiting viscosity number was found. All determinations should consequently be performed on samples containing at least 50 pellets or one gram of polymer (or material from a blend of one gram). This will reduce the expectation of the standard error due to pellet variability to less than 0.5 percent.

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 gel-permeation 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.

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.

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

T	C_p(0.954,T)	C_p(1.000,T)	ΔC(T)	T	C_p(0.954,T)	C_p(1.000,T)	ΔC(T)
K	J/(mol·K)			K	J/(mol·K)		
5	0.024	0.014	0.038	190	15.98	14.87	3.94
10	.173	.106	.235	200	16.66	15.47	4.25
15	.473	.342	.458	210	17.36	16.08	4.58
20	.904	.727	.619	220	18.10	16.70	5.00
25	1.433	1.231	.706	230	18.91	17.35	5.55
30	2.027	1.819	.728	240	19.80	18.03	6.29
35	2.664	2.465	.702	250	20.76	18.72	7.22
40	3.322	3.135	.652	260	21.76	19.45	8.19
45	3.981	3.811	.587	270	22.78	20.23	9.06
50	4.626	4.475	.516	280	23.80	21.04	9.81
60	5.841	5.730	.385	290	24.83	21.89	10.47
70	6.935	6.855	.288	300	25.87	22.76	11.09
80	7.911	7.847	.230	310	26.95	23.64	11.80
90	8.786	8.725	.208	320	28.11	24.54	12.72
100	9.579	9.511	.226	330	29.39	25.46	13.97
110	10.31	10.23	.30	340	30.86	26.46	15.63
120	11.01	10.88	.47	350	32.59	27.57	17.76
130	11.70	11.49	.78	360	34.65	28.90	20.31
140	12.44	12.07	1.31				
150	13.18	12.62	1.98	273.15	23.10	20.48	9.31
160	13.91	13.17	2.61				
170	14.61	13.73	3.15	298.15	25.68	22.60	10.93
180	15.30	14.30	3.59				

Heat capacities C_p (ρ, T) at various temperatures are given at two 23 °C densities, $\rho = 0.954$ and $\rho = 1.000$ g/cm^3 in Table 2. These density values differ from the value certified in this certificate, which was obtained after carrying out ASTM Procedure A, ASTM Method D1928-70 for sample preparation. The density of the sample as received was 0.954 g/cm^3, but 4 years later following these tests had increased to 0.958 g/cm^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 ΔC(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 (ρ, T) are believed to be less than 1% between 25 and 360 K and increase to about 5% at 5 K.

Reports describing investigations required for the certification of this Standard Reference Material are published in the Journal of Research of the National Bureau of Standards **76A,** 137-170 (1972), **77A,** 395-405 (1973) and **78A,** 387-400 (1974).