National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2490

Non-Newtonian Polymer Solution for Rheology

Polyisobutylene Dissolved in 2,6,10,14-Tetramethylpentadecane

This Standard Reference Material (SRM) is intended primarily for use in calibration and performance evaluation of instruments used to determine the viscosity and first normal stress difference in steady shear, or to determine the dynamic mechanical storage and loss moduli and shift factors through time-temperature superposition. SRM 2490 consists of a polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane (common name pristane). The solution contains a mass fraction of 0.114 polyisobutylene. The mass average relative molecular mass of the polyisobutylene is reported as 1 000 000 by the supplier. One unit of SRM 2490 consists of 100 mL of the solution packaged in an amber glass bottle.

Certified Values and Uncertainties: The certified values of the viscosity and first normal stress difference as functions of shear rate are given in Tables 4a, 4b, and 4c at temperatures of 0 °C, 25 °C, and 50 °C, respectively. Tables 4a through 4c also list the expanded combined uncertainties in the certified values of the viscosity and first normal stress difference. Tables 5a, 5b, 5c, 5d, 5e, and 5f list the certified values of the storage modulus G' and loss modulus G'' as functions of frequency at 0 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C, respectively. Tables 5a through 5f also list the expanded combined uncertainties in the certified values of the storage modulus G' and loss modulus G''. The uncertainties in Tables 4a through 4c and 5a through 5f were calculated as $U = ku_c$, where $k = 2$ is the coverage factor for a 95 % level of confidence and u_c is the combined standard uncertainty calculated according to the ISO Guide [1].

Expiration of Certification: The certification of SRM 2490 is valid until **31 December 2008**, within the measurement uncertainties specified, provided that the SRM is handled in accordance with the storage instructions given in this certificate. This certification is nullified if the SRM is modified or contaminated.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Technical coordination leading to the certification of this SRM was provided by B.M. Fanconi of the NIST Polymers Division.

The certification of this SRM was performed by C.R. Schultheisz of the NIST Polymers Division.

The support aspects in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.W.L. Thomas.

Eric J. Amis, Chief
Polymers Division

Gaithersburg, MD 20899
Certificate Issue Date: 18 September 2001

John Rumble, Jr., Acting Chief
Standard Reference Materials Program

Statistical analysis and measurement advice were provided by S.D. Leigh of the NIST Statistical Engineering Division.

Technical assistance and advice were provided by Gregory Strouse and Dawn Vaughn of the NIST Process Measurements Division and Gregory B. McKenna of the Texas Tech University.

Source of Material: The polyisobutylene and 2,6,10,14-tetramethylpentadecane were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin.[1] The solution was mixed and packaged by the Cannon Instrument Company, State College, PA.[1]

Storage and Handling: The SRM should be stored in the original bottle with the lid tightly closed under normal laboratory conditions. Before taking a sample, the bottle should be turned end-over-end at a rate of approximately 1 revolution per 10 minutes for 30 minutes. This procedure is intended to ensure that the material in each bottle is homogeneous, in case there is any settling caused by gravity.

Homogeneity and Characterization: The homogeneity of SRM 2490 was tested by measuring the zero-shear-rate viscosity at 25 °C from 10 bottles randomly chosen from the 438 bottles available. Three samples from each bottle were tested in random order. The characterization of this polymer solution is described in reference [2].

Measurement Technique: All rheological testing was carried out using a Rheometric Scientific, Inc., ARES controlled-strain rheometer.[1] Transducer calibration was accomplished, in accordance with the manufacturer's instructions, by hanging a known mass from a fixture mounted to the transducer to apply a known torque or normal force. Phase angle calibration was accomplished, also in accordance with the manufacturer's instructions, by applying an oscillatory strain to an elastic steel test coupon. Temperature calibration in the rheometer was accomplished through comparison with a NIST-calibrated thermistor. The viscosity and first normal stress difference were measured in steady shear using 50 mm diameter, 0.02 rad cone-and-plate fixtures. The storage modulus and loss modulus were measured in 50 mm diameter parallel-plate fixtures with an applied strain magnitude of 20 % at a nominal gap of 1 mm.

Models for the Data: The steady shear data (viscosity and first normal stress difference) and the oscillatory data (storage modulus and loss modulus) were fitted to empirical functions to describe master curves and calculate shift factors for time-temperature superposition. These models can be used to estimate the rheological behavior of the material in the temperature range 0 °C to 50 °C.

Models for the Steady Shear Data: The viscosity $\eta(\dot{\gamma},T)$ as a function of the shear rate $\dot{\gamma}$, and the temperature T was fitted to a Cross model [3,4] of the form

$$\eta(\dot{\gamma},T)=\left(\frac{T\rho}{T_R\rho_R}\right)\left(\frac{\eta_R a(T)}{1+(\xi_0 a(T)\dot{\gamma})^{1-n}}\right) \tag{1}$$

where ρ is the density at temperature T, η_R is the zero-shear-rate viscosity at the reference temperature T_R = 25 °C, ρ_R is the density at the reference temperature T_R, ξ_0 is a parameter that governs the transition from the Newtonian regime at low shear rates to the power law regime at high shear rates, and n is the power at which the shear stress increases with shear rate. The density was approximated as a linear function of temperature, with $\rho(T)=\rho_R(1-\alpha(T-T_R))$, where α = 6 × 10^{-4} $cm^3/(cm^3$ K) is the volumetric coefficient of thermal expansion. The shift factor $a(T)$ was fitted with a function of the WLF type [3],

$$a(T)=\exp\left(\frac{-C_1(T-T_R)}{C_2+T-T_R}\right) \tag{2}$$

[1]Certain commercial equipment, instrumentation, or materials are identified in this certificate to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

The parameters η_R, ξ_0, n, C_1, and C_2 estimated from the fit to the viscosity data are given in Table 1.

Table 1. Parameters for $\eta(\dot{\gamma},T)$ and $a(T)$

Parameter	Value	Standard Uncertainty
η_R	100.2 Pa·s	0.6 Pa·s
ξ_0	0.234 s	0.004 s
n	0.195	0.004
C_1	7.23	0.24
C_2	150 °C	5 °C

The first normal stress difference $N_1(\dot{\gamma},T)$ was fitted to a similar empirical model using the same temperature shift factor $a(T)$ calculated from the viscosity data:

$$N_1(\dot{\gamma},T) = \left(\frac{T\rho}{T_R\rho_R}\right)\left(\frac{\psi_R(a(T)\dot{\gamma})^2}{1+\xi_1 a(T)\dot{\gamma}+(\xi_2 a(T)\dot{\gamma})^p}\right) \tag{3}$$

where ρ is the density at temperature T; ψ_R is the zero-shear-rate first normal stress coefficient at the reference temperature T_R = 25 °C; ρ_R is the density at the reference temperature T_R; and ξ_1, ξ_2, and p are parameters estimated from the fit to the data. The density was approximated as a linear function of temperature, with $\rho(T)=\rho_R(1-\alpha(T-T_R))$, where α = 6 × 10^{-4} $cm^3/(cm^3$ K). Values for the parameters describing $N_1(\dot{\gamma},T)$ are given in Table 2.

Table 2. Parameters for $N_1(\dot{\gamma},T)$

Parameter	Value	Standard Uncertainty
ψ_R	129 Pa·s^2	5 Pa·s^2
ξ_1	1.69 s	0.13 s
ξ_2	0.247 s	0.026 s
p	1.67	0.047

Models for the Oscillatory Data: The storage modulus G'(Ω,T) and loss modulus G''(Ω,T) as functions of the frequency of oscillation Ω and temperature T were modeled using polynomial functions [4]. The data were fitted to functions of the form

$$\begin{aligned}\ln\left(\frac{G'(\Omega,T)}{1\ \mathrm{Pa}}\right) &= \ln\left(\frac{T\rho}{T_R\rho_R}\right)+\sum_{k=0}^{4} p_k\left(\ln\left(\frac{a(T)\Omega}{1\ \mathrm{rad/s}}\right)\right)^k \\ \ln\left(\frac{G''(\Omega,T)}{1\ \mathrm{Pa}}\right) &= \ln\left(\frac{T\rho}{T_R\rho_R}\right)+\sum_{k=0}^{4} q_k\left(\ln\left(\frac{a(T)\Omega}{1\ \mathrm{rad/s}}\right)\right)^k\end{aligned} \tag{4}$$

where ρ is the density at temperature T, and ρ_R is the density at the reference temperature $T_R = 25$ °C. The density was again approximated as a linear function of temperature, with $\rho(T) = \rho_R(1-\alpha(T-T_R))$, where $\alpha = 6 \times 10^{-4}$ cm^3/(cm^3 K). The shift factor $a(T)$ again was fitted with a function of the WLF type [3],

$$a(T) = \exp\left(\frac{-C_1(T-T_R)}{C_2+T-T_R}\right) \tag{5}$$

The parameters estimated from the to the oscillatory data are given in Table 3.

Table 3. Parameters for $G'(\Omega,T)$, $G''(\Omega,T)$ and $a(T)$

Parameter	Value	Standard Uncertainty
p_0	3.177	0.005
p_1	1.235	0.003
p_2	− 0.134	0.001
p_3	2.36×10^{-3}	2.7×10^{-4}
p_4	5.20×10^{-4}	6.1×10^{-5}
q_0	4.196	0.005
q_1	0.720	0.003
q_2	− 0.0719	0.0011
q_3	-3.18×10^{-3}	2.6×10^{-4}
q_4	7.06×10^{-4}	6.0×10^{-5}
C_1	8.85	0.30
C_2	192 °C	6 °C

Table 4a. Certified Values of Viscosity and First Normal Stress Difference with Expanded Combined Uncertainties at 0 °C

Temperature	Shear Rate	Certified Value of the Viscosity, η	Uncertainty in the Viscosity	Certified Value of the First Normal Stress Difference, N_1	Uncertainty in N_1
°C	s^{-1}	Pa·s	Pa·s	Pa	Pa
0.0	0.001000	383	12		
0.0	0.001585	380	11		
0.0	0.002512	382.4	9.9		
0.0	0.003981	382.9	9.5		
0.0	0.006310	384.0	9.2		
0.0	0.01000	383.1	9.0		
0.0	0.01585	382.9	8.8		
0.0	0.02512	379.8	8.6		
0.0	0.03981	375.1	8.3		
0.0	0.06310	365.5	7.9		
0.0	0.1000	350.0	7.3		
0.0	0.1585	328.4	6.6	16	11
0.0	0.2512	300.8	5.7	44	10
0.0	0.3981	268.5	4.8	92	11
0.0	0.6310	233.0	3.8	149	14
0.0	1.000	196.5	2.9	257	15
0.0	1.585	161.1	2.1	372	15
0.0	2.512	128.4	1.5	573	17
0.0	3.981	99.45	0.98	845	21
0.0	6.310	75.07	0.66	1219	29
0.0	10.00	55.59	0.44	1717	35
0.0	15.85	40.26	0.29	2363	44
0.0	25.12	28.67	0.20	3196	55
0.0	39.81	20.23	0.17	4251	69
0.0	63.10	13.88	0.15	5519	87
0.0	100.0	9.08	0.12	7126	107

Table 4b. Certified Values of Viscosity and First Normal Stress Difference with Expanded Combined Uncertainties at 25 °C

Temperature	Shear Rate	Certified Value of the Viscosity, η	Uncertainty in the Viscosity	Certified Value of the First Normal Stress Difference, N_1	Uncertainty in N_1
°C	s^{-1}	Pa·s	Pa·s	Pa	Pa
25.0	0.001000	97.9	7.0		
25.0	0.001585	98.1	4.9		
25.0	0.002512	98.3	3.7		
25.0	0.003981	97.9	2.9		
25.0	0.006310	98.4	2.5		
25.0	0.01000	98.1	2.3		
25.0	0.01585	98.7	2.2		
25.0	0.02512	98.8	2.2		
25.0	0.03981	98.6	2.1		
25.0	0.06310	98.4	2.1		
25.0	0.1000	97.5	2.0		
25.0	0.1585	96.1	2.0	2.4	1.9
25.0	0.2512	93.7	1.9	5.5	1.8
25.0	0.3981	90.0	1.8	12.9	1.9
25.0	0.6310	84.6	1.6	26.5	2.1
25.0	1.000	77.6	1.4	50.1	2.5
25.0	1.585	69.2	1.2	87.6	3.3
25.0	2.512	59.98	0.94	148.2	4.6
25.0	3.981	50.56	0.72	236.8	7.4
25.0	6.310	41.44	0.54	377	12
25.0	10.00	33.04	0.39	585	16
25.0	15.85	25.60	0.28	880	21
25.0	25.12	19.36	0.20	1280	27
25.0	39.81	14.26	0.15	1800	36
25.0	63.10	10.22	0.14	2462	51
25.0	100.0	7.22	0.13	3319	63

Table 4c. Certified Values of Viscosity and First Normal Stress Difference with Expanded Combined Uncertainties at 50 °C

Temperature	Shear Rate	Certified Value of the Viscosity, η	Uncertainty in the Viscosity	Certified Value of the First Normal Stress Difference, N_1	Uncertainty in N_1
°C	s^{-1}	Pa·s	Pa·s	Pa	Pa
50.0	0.001000	36.7	6.5		
50.0	0.001585	37.2	4.2		
50.0	0.002512	37.6	2.8		
50.0	0.003981	37.3	2.0		
50.0	0.006310	37.7	1.5		
50.0	0.01000	37.7	1.3		
50.0	0.01585	37.5	1.1		
50.0	0.02512	37.5	1.1		
50.0	0.03981	37.8	1.1		
50.0	0.06310	37.8	1.1		
50.0	0.1000	37.8	1.1		
50.0	0.1585	37.7	1.1		
50.0	0.2512	37.4	1.1		
50.0	0.3981	36.9	1.1	2.4	1.7
50.0	0.6310	36.1	1.1	5.1	1.7
50.0	1.000	34.8	1.0	10.7	1.8
50.0	1.585	32.79	0.99	21.5	2.0
50.0	2.512	30.20	0.93	41.0	2.7
50.0	3.981	27.05	0.84	68.8	4.3
50.0	6.310	23.54	0.74	114.5	7.6
50.0	10.00	19.95	0.64	203	11
50.0	15.85	16.41	0.53	345	16
50.0	25.12	13.14	0.43	558	23
50.0	39.81	10.24	0.34	860	33
50.0	63.10	7.75	0.26	1269	47
50.0	100.0	5.72	0.20	1797	67

Table 5a. Certified Values of the Storage Modulus G' and the Loss Modulus G'' with Expanded Combined Uncertainties at 0 °C

Temperature	Frequency of Oscillation	Certified Value of the Storage Modulus G'	Uncertainty in G'	Certified Value of the Loss Modulus G''	Uncertainty in G''
°C	rad/s	Pa	Pa	Pa	Pa
0.0	0.02512	0.605	0.058	7.98	0.15
0.0	0.03981	1.385	0.090	12.35	0.23
0.0	0.06310	2.97	0.14	18.85	0.35
0.0	0.1000	6.07	0.23	28.20	0.51
0.0	0.1585	11.70	0.37	41.11	0.73
0.0	0.2512	21.21	0.58	58.3	1.0
0.0	0.3981	36.21	0.88	79.8	1.4
0.0	0.6310	58.5	1.3	105.9	1.8
0.0	1.000	89.6	1.9	135.6	2.3
0.0	1.585	130.9	2.5	168.1	2.9
0.0	2.512	183.0	3.4	201.9	3.5
0.0	3.981	246.1	4.4	235.9	4.1
0.0	6.310	319.8	5.5	268.8	4.8
0.0	10.00	403.3	6.8	299.7	5.4
0.0	15.85	495.3	8.1	328.1	6.1
0.0	25.12	593.8	9.7	354.1	6.8
0.0	39.81	697	11	378.9	7.6
0.0	63.10	804	13	404.1	8.3
0.0	100.0	913	15	432.1	9.2

Table 5b. Certified Values of the Storage Modulus G' and the Loss Modulus G'' with Expanded Combined Uncertainties at 10 °C

Temperature	Frequency of Oscillation	Certified Value of the Storage Modulus G'	Uncertainty in G'	Certified Value of the Loss Modulus G''	Uncertainty in G''
°C	rad/s	Pa	Pa	Pa	Pa
10.0	0.03981	0.486	0.052	7.29	0.13
10.0	0.06310	1.099	0.082	11.35	0.21
10.0	0.1000	2.44	0.13	17.42	0.31
10.0	0.1585	5.08	0.20	26.29	0.47
10.0	0.2512	10.02	0.33	38.73	0.68
10.0	0.3981	18.53	0.52	55.45	0.95
10.0	0.6310	32.33	0.80	76.9	1.3
10.0	1.000	53.2	1.2	103.2	1.7
10.0	1.585	83.2	1.7	133.7	2.2
10.0	2.512	123.3	2.4	167.6	2.8
10.0	3.981	174.8	3.2	203.4	3.4
10.0	6.310	238.2	4.2	240.1	4.1
10.0	10.00	313.2	5.3	276.1	4.8
10.0	15.85	398.8	6.7	310.3	5.5
10.0	25.12	493.9	8.1	342.2	6.3
10.0	39.81	596.4	9.7	372.0	7.0
10.0	63.10	704	11	400.7	7.8
10.0	100.0	816	13	429.9	8.7

Table 5c. Certified Values of the Storage Modulus G' and the Loss Modulus G''
with Expanded Combined Uncertainties at 20 °C

Temperature	Frequency of Oscillation	Certified Value of the Storage Modulus G'	Uncertainty in G'	Certified Value of the Loss Modulus G''	Uncertainty in G''
°C	rad/s	Pa	Pa	Pa	Pa
20.0	0.03981	0.182	0.034	4.605	0.083
20.0	0.06310	0.430	0.053	7.26	0.13
20.0	0.1000	1.023	0.080	11.28	0.20
20.0	0.1585	2.27	0.13	17.38	0.30
20.0	0.2512	4.81	0.20	26.30	0.45
20.0	0.3981	9.57	0.32	38.91	0.66
20.0	0.6310	17.92	0.50	56.01	0.94
20.0	1.000	31.62	0.78	78.2	1.3
20.0	1.585	52.6	1.2	105.5	1.7
20.0	2.512	82.7	1.7	137.5	2.2
20.0	3.981	123.8	2.4	173.3	2.8
20.0	6.310	176.8	3.2	211.6	3.5
20.0	10.00	242.5	4.2	251.0	4.2
20.0	15.85	320.6	5.4	290.1	4.9
20.0	25.12	410.4	6.7	327.5	5.7
20.0	39.81	510.1	8.2	363.0	6.5
20.0	63.10	617.8	9.8	396.8	7.3
20.0	100.0	731	12	429.7	8.2

Table 5d. Certified Values of the Storage Modulus G' and the Loss Modulus G'' with Expanded Combined Uncertainties at 30 °C

Temperature	Frequency of Oscillation	Certified Value of the Storage Modulus G'	Uncertainty in G'	Certified Value of the Loss Modulus G''	Uncertainty in G''
°C	rad/s	Pa	Pa	Pa	Pa
30.0	0.03981	0.077	0.023	3.028	0.055
30.0	0.06310	0.178	0.036	4.773	0.084
30.0	0.1000	0.440	0.054	7.48	0.13
30.0	0.1585	1.039	0.082	11.65	0.20
30.0	0.2512	2.32	0.13	17.94	0.31
30.0	0.3981	4.90	0.21	27.17	0.46
30.0	0.6310	9.78	0.33	40.19	0.68
30.0	1.000	18.38	0.52	57.92	0.96
30.0	1.585	32.46	0.80	80.9	1.3
30.0	2.512	54.0	1.2	109.2	1.8
30.0	3.981	85.2	1.7	142.6	2.3
30.0	6.310	127.7	2.5	180.0	2.9
30.0	10.00	182.6	3.3	220.0	3.6
30.0	15.85	250.7	4.4	261.3	4.3
30.0	25.12	331.7	5.6	302.3	5.1
30.0	39.81	424.5	7.0	342.1	5.9
30.0	63.10	527.3	8.6	380.4	6.8
30.0	100.0	638	10	417.2	7.6

Table 5e. Certified Values of the Storage Modulus G' and the Loss Modulus G'' with Expanded Combined Uncertainties at 40 °C

Temperature	Frequency of Oscillation	Certified Value of the Storage Modulus G'	Uncertainty in G'	Certified Value of the Loss Modulus G''	Uncertainty in G''
°C	rad/s	Pa	Pa	Pa	Pa
40.0	0.03981	0.030	0.019	2.047	0.039
40.0	0.06310	0.062	0.025	3.236	0.063
40.0	0.1000	0.200	0.038	5.101	0.096
40.0	0.1585	0.478	0.055	8.00	0.15
40.0	0.2512	1.142	0.088	12.45	0.23
40.0	0.3981	2.56	0.14	19.16	0.36
40.0	0.6310	5.39	0.22	28.94	0.54
40.0	1.000	10.69	0.36	42.76	0.80
40.0	1.585	19.97	0.57	61.4	1.1
40.0	2.512	35.03	0.89	85.5	1.6
40.0	3.981	58.0	1.4	115.1	2.1
40.0	6.310	91.0	2.0	149.8	2.8
40.0	10.00	135.7	2.8	188.5	3.5
40.0	15.85	193.2	3.9	229.7	4.3
40.0	25.12	264.1	5.1	272.2	5.1
40.0	39.81	347.7	6.6	314.6	6.0
40.0	63.10	443.1	8.3	356.1	6.9
40.0	100.0	548	10	396.3	7.9

Table 5f. Certified Values of the Storage Modulus G' and the Loss Modulus G'' with Expanded Combined Uncertainties at 50 °C

Temperature	Frequency of Oscillation	Certified Value of the Storage Modulus G'	Uncertainty in G'	Certified Value of the Loss Modulus G''	Uncertainty in G''
°C	rad/s	Pa	Pa	Pa	Pa
50.0	0.03981	0.013	0.017	1.457	0.034
50.0	0.06310	0.034	0.021	2.316	0.058
50.0	0.1000	0.088	0.028	3.63	0.092
50.0	0.1585	0.241	0.041	5.73	0.15
50.0	0.2512	0.592	0.063	8.98	0.23
50.0	0.3981	1.37	0.10	13.95	0.37
50.0	0.6310	3.06	0.17	21.39	0.56
50.0	1.000	6.39	0.28	32.21	0.85
50.0	1.585	12.51	0.46	47.3	1.2
50.0	2.512	23.03	0.77	67.6	1.8
50.0	3.981	40.0	1.2	93.5	2.5
50.0	6.310	65.4	1.9	125.0	3.3
50.0	10.00	101.5	2.9	161.6	4.3
50.0	15.85	149.8	4.2	202.0	5.3
50.0	25.12	211.6	5.8	245.0	6.5
50.0	39.81	286.6	7.8	289.0	7.7
50.0	63.10	375	10	333.1	9.0
50.0	100.0	474	13	376	10

REFERENCES

[1] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993); see also Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington, DC, (1994); available at http://physics.nist.gov/Pubs/.

[2] Schultheisz, C.R. and Leigh, S.J., "Certification of the Rheological Behavior of SRM 2490, Polyisobutylene Dissolved in 2,6,10,14-Tetramethylpentadecane," NIST Special Publication 260-143, U.S. Department of Commerce, Technology Administration, National Institute of Standards and Technology, (2001).

[3] Macosko, C.W., *Rheology - Principles, Measurements and Applications*, Wiley-VCH, New York, (1994).

[4] Gordon, G.V. and Shaw, M.T., *Computer Programs for Rheologists*, Hanser Publishers, Munich, (1994).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.