Solution Viscosity of Polystyrene at Conditions Applicable to Commercial Manufacturing Processes

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Literature data and previously unpublished results were correlated for polystyrene solutions at temperatures, compositions, and shear rates applicable to commercial practice. The primary correlation is for the zero shear viscosity and includes 222 points within the following ranges: temperature, T/K, 293–513; weight-average molecular weight, M_w, 52000–381000; polydispersity, P_d, 1.01–5.2; weight fraction of polymer, W_p, 0.06–1.0. A secondary correlation for apparent viscosity as a function of shear rate is based on 344 additional points with shear rates from 0.01 to 28221 s^{-1}.

Introduction

There is substantial industrial and academic interest in the modeling of styrene polymerization processes. One necessary component of such models is a viscosity correlation which spans the region of commercial interest. A correlation is particularly needed to study polymerizations in tubular geometries where viscosity gradients can have a pronounced effect on velocity profiles (*1*).

Spencer and Williams (*2*) measured low shear viscosities of polystyrene in isopropylbenzene. Their result can be stated as

$$\ln(\mu_0/(\text{Pa·s})) = -28.64 + 0.057 M_w^{0.5} + W_p^{0.5}(22.54 - 0.045 M_w^{0.5} + 5000/(T/\text{K})) \quad (1)$$

where μ_0 is the zero shear viscosity. Their data extended to only 373 K and thus excluded the region of major commercial importance where temperatures are generally above 373 K for polymerization by thermal initiation and up to 523 K for reaction during devolatilization. Subsequent to Spencer and Williams, several other correlations were proposed (*3*–*8*), but these too lacked relevance to most industrial processes. A more useful correlation for process modeling was developed by Harkness (*9*):

$$\ln(\mu_0/(\text{Pa·s})) = -13.04 + 2013/(T/\text{K}) + M_w^{0.18}[3.915 W_p - 5.437 W_p^2 + (0.623 + 1387/(T/\text{K})) W_p^3] \quad (2)$$

This result was used in the modeling studies of Agawal (*10*), Chen and Nauman (*11*), and Mallikarjun and Nauman (*12*, *13*). The data base used by Harkness generally spans the region of industrial interest, but his correlation does not include effects due to polydispersity or to nonzero shear rates. The present study includes these factors and updates the literature survey of Harkness. A total of 14 sources were used. The data and citations are provided in Tables I and II. Some of the data cited are from private communications and thus not otherwise available in the archival literature.

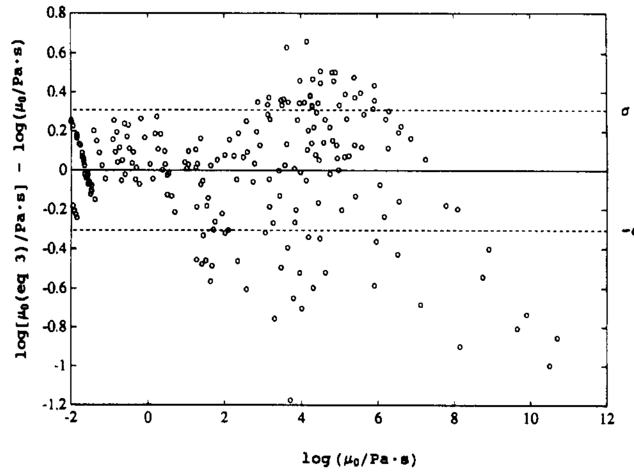

Figure 1. Deviation between experimental and predicted values of zero shear viscosity.

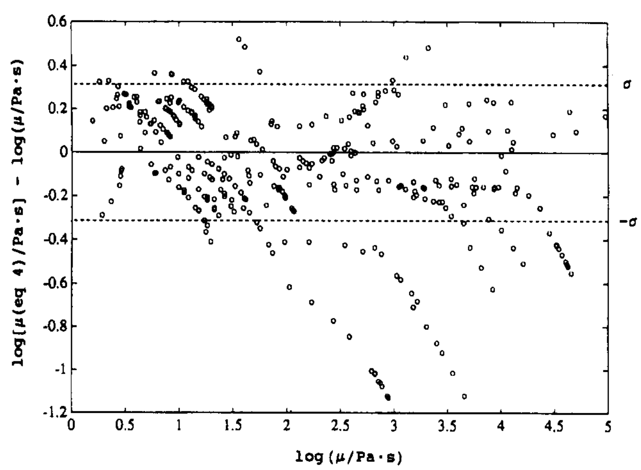

Figure 2. Deviation between experimental and predicted values of apparent viscosity.

Zero Shear Correlation

A nonlinear, least-squares minimization technique was applied to the zero shear data in Table I. The final result was

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Table I. Data for Zero Shear Viscosity μ_0 ($\delta\mu_0$ Is the Ratio of Values Calculated from Equation 3 to Experimental Values)

$10^{-3}M_W/(g\ mol^{-1})$	P_d	W_p	T/K	$\log(\mu_0/(Pa \cdot s))$	$\log \delta\mu_0$	ref	$10^{-3}M_W/(g\ mol^{-1})$	P_d	W_p	T/K	$\log(\mu_0/(Pa \cdot s))$	$\log \delta\mu_0$	ref
142	1.90	0.10	298.0	−2.0000	0.2470	18	366	2.14	0.41	333.0	1.0000	0.0108	26
148	1.90	0.10	298.0	−2.0000	0.2555	18	259	2.35	0.50	384.0	1.0414	0.0313	24
158	1.90	0.10	298.0	−1.9586	0.2276	18	307	2.65	0.60	446.0	1.0414	0.0995	9
366	2.14	0.06	313.0	−1.9586	−0.1827	26	366	2.14	0.45	333.0	1.2304	0.0154	26
366	2.14	0.06	308.0	−1.9208	−0.2060	26	307	2.65	0.60	424.0	1.2304	0.1081	9
366	2.14	0.06	303.0	−1.8861	−0.2257	26	307	2.65	0.70	503.0	1.2553	−0.4556	9
366	2.14	0.06	298.0	−1.8539	−0.2425	26	366	2.14	0.41	313.0	1.2553	−0.1874	26
193	1.80	0.10	298.0	−1.8539	0.1650	18	366	2.14	0.46	333.0	1.2788	0.0337	26
210	2.60	0.10	298.0	−1.8539	0.1832	18	366	2.14	0.45	323.0	1.3617	−0.0717	26
203	3.50	0.10	298.0	−1.8539	0.1759	18	307	2.65	0.60	405.0	1.3617	0.1647	9
220	4.20	0.10	298.0	−1.7959	0.1353	18	307	2.65	0.70	493.0	1.3979	−0.4775	9
243	3.40	0.10	298.0	−1.7696	0.1308	18	366	2.14	0.46	323.0	1.4150	−0.0532	26
253	2.70	0.10	298.0	−1.7212	0.0913	18	366	2.14	0.41	303.0	1.4314	−0.3321	26
232	2.10	0.10	298.0	−1.7212	0.0722	18	307	2.65	0.70	483.0	1.5051	−0.4589	9
252	2.80	0.10	298.0	−1.6990	0.0682	18	366	2.14	0.45	313.0	1.5185	−0.1815	26
266	2.70	0.10	298.0	−1.6778	0.0590	18	366	2.14	0.46	313.0	1.5563	−0.1420	26
250	2.33	0.10	298.0	−1.6778	0.0452	17	259	2.35	0.70	473.0	1.6232	−0.5642	24
256	2.70	0.10	298.0	−1.6778	0.0505	18	271	2.50	0.65	410.0	1.6232	0.0260	30
366	2.14	0.09	323.0	−1.6576	−0.0189	26	307	2.65	0.70	473.0	1.6628	−0.4855	9
251	2.20	0.10	298.0	−1.6576	0.0259	18	366	2.14	0.45	303.0	1.6902	−0.3031	26
366	2.14	0.09	313.0	−1.6198	−0.0379	26	366	2.14	0.46	303.0	1.7324	−0.2621	26
279	2.60	0.10	298.0	−1.5850	−0.0231	18	271	2.50	0.65	395.0	1.7993	0.0546	30
288	3.00	0.10	298.0	−1.5850	−0.0159	18	366	2.14	0.51	333.0	1.9138	−0.2208	26
280	2.50	0.10	298.0	−1.5850	−0.0223	18	271	2.50	0.65	380.0	1.9956	0.0792	30
269	2.90	0.10	298.0	−1.5850	−0.0313	18	259	2.35	0.70	430.0	2.0000	−0.3205	24
273	1.90	0.10	298.0	−1.5850	−0.0279	18	366	2.14	0.51	323.0	2.0792	−0.3049	26
266	2.90	0.10	298.0	−1.5850	−0.0338	18	79	1.10	1.00	490.3	2.1139	0.1597	23
297	5.20	0.10	298.0	−1.5850	−0.0089	18	271	2.50	0.65	365.5	2.2304	0.0751	30
289	3.10	0.10	298.0	−1.5850	−0.0151	18	271	2.50	0.76	428.0	2.3010	−0.0451	30
304	2.50	0.10	298.0	−1.5686	−0.0200	18	366	2.14	0.51	313.0	2.3222	−0.4613	26
366	2.14	0.09	303.0	−1.5686	−0.0690	26	79	1.10	1.00	482.9	2.3424	0.1889	23
296	2.90	0.10	298.0	−1.5376	−0.0571	18	271	2.50	0.65	351.5	2.4771	0.0693	30
299	2.09	0.10	298.0	−1.5229	−0.0693	17	366	2.14	0.51	303.0	2.5563	−0.6032	26
366	2.14	0.09	293.0	−1.4949	−0.1213	26	79	1.10	1.00	475.2	2.5563	0.2516	23
315	2.60	0.10	298.0	−1.4815	−0.0990	18	271	2.50	0.76	409.5	2.5798	0.0947	30
366	2.14	0.10	298.0	−1.4685	−0.0773	17	307	2.65	1.00	513.0	2.7243	−0.0569	9
322	2.50	0.10	298.0	−1.4685	−0.1070	18	271	2.50	0.65	337.5	2.7709	0.0363	30
366	2.14	0.13	333.0	−1.4089	0.2033	26	271	2.50	0.76	395.5	2.8195	0.1977	30
381	2.00	0.10	298.0	−1.3872	−0.1492	18	79	1.10	1.00	464.7	2.8513	0.3486	23
366	2.14	0.13	323.0	−1.3468	0.1510	26	271	2.50	0.82	424.5	2.9085	0.1305	30
366	2.14	0.13	313.0	−1.2757	0.0904	26	193	1.06	1.00	500.0	3.0414	−0.3195	28
366	2.14	0.13	303.0	−1.2007	0.0265	26	307	2.65	1.00	493.0	3.1139	0.3345	9
366	2.14	0.13	293.0	−1.1192	−0.0431	26	271	2.50	0.76	381.0	3.1139	0.2848	30
366	2.14	0.17	323.0	−0.9208	0.1594	26	271	2.50	0.93	472.5	3.1461	−0.1856	30
366	2.14	0.18	333.0	−0.8861	0.2565	26	79	1.10	1.00	456.5	3.1461	0.3725	23
366	2.14	0.17	313.0	−0.8539	0.0962	26	271	2.50	0.65	323.0	3.1461	−0.0449	30
366	2.14	0.18	323.0	−0.8239	0.1961	26	271	2.50	0.82	411.0	3.1761	0.2611	30
366	2.14	0.17	303.0	−0.7959	0.0421	26	193	1.07	1.00	493.0	3.2553	−0.2698	28
366	2.14	0.18	313.0	−0.7447	0.1188	26	259	2.35	0.90	473.0	3.3010	−0.7557	24
366	2.14	0.17	293.0	−0.6990	−0.0506	26	271	2.50	0.93	460.0	3.3979	0.0004	30
366	2.14	0.18	303.0	−0.6778	0.0539	26	271	2.50	0.65	314.5	3.4150	−0.1288	30
366	2.14	0.21	333.0	−0.6198	0.2398	26	79	1.10	1.00	449.0	3.4624	0.3578	23
366	2.14	0.18	293.0	−0.6021	−0.0197	26	250	2.33	1.00	500.0	3.4624	−0.4956	17
366	2.14	0.21	323.0	−0.5528	0.1720	26	271	2.50	0.76	366.0	3.4914	0.3338	30
366	2.14	0.22	333.0	−0.5229	0.2320	26	271	2.50	0.82	396.5	3.5315	0.3635	30
366	2.14	0.21	313.0	−0.4949	0.1133	26	160	1.05	1.00	473.0	3.5563	0.0269	28
366	2.14	0.21	303.0	−0.4202	0.0377	26	271	2.50	0.93	450.5	3.6128	0.1344	30
366	2.14	0.22	313.0	−0.3872	0.0934	26	307	2.65	1.00	474.0	3.6232	0.6283	9
366	2.14	0.21	293.0	−0.3372	−0.0462	26	250	2.33	1.00	493.0	3.6335	−0.3939	17
366	2.14	0.22	303.0	−0.3098	0.0144	26	79	1.10	1.00	444.6	3.6532	0.3487	23
366	2.14	0.22	293.0	−0.2291	−0.0680	26	265	2.17	1.00	513.0	3.7076	−1.1752	33
366	2.14	0.26	333.0	−0.1871	0.2655	26	299	2.09	1.00	500.0	3.7924	−0.6499	30
366	2.14	0.26	323.0	−0.0915	0.1679	26	193	1.07	1.00	472.0	3.8129	0.0101	23
366	2.14	0.26	313.0	0.0414	0.0329	26	271	2.50	0.65	303.0	3.8195	−0.2666	30
366	2.14	0.26	303.0	0.1139	−0.0419	26	250	2.33	1.00	483.0	3.8451	−0.2020	17
366	2.14	0.30	333.0	0.1761	0.1873	26	271	2.50	0.93	440.0	3.8921	0.2583	7
366	2.14	0.33	333.0	0.2304	0.2742	26	299	2.09	1.00	493.0	3.9445	−0.5225	17
366	2.14	0.30	323.0	0.2553	0.1092	26	271	2.50	0.76	351.0	3.9445	0.3437	30
366	2.14	0.33	323.0	0.3222	0.1869	26	271	2.50	0.82	381.0	3.9638	0.4592	30
366	2.14	0.30	313.0	0.3617	0.0041	26	271	2.50	1.00	477.5	3.9685	−0.0082	30
366	2.14	0.33	313.0	0.4150	0.0988	26	265	2.17	1.00	493.0	4.0000	−0.7018	33
366	2.14	0.32	323.0	0.4314	0.0322	26	179	1.07	1.00	456.0	4.0792	0.3461	11
366	2.14	0.30	303.0	0.4914	−0.1243	26	250	2.33	1.00	473.0	4.1139	−0.0502	17
366	2.14	0.32	313.0	0.4914	−0.0243	26	220	3.10	1.00	453.0	4.1461	0.6584	12
366	2.14	0.33	303.0	0.5315	−0.0127	26	179	1.01	1.00	460.0	4.1461	0.1059	11
366	2.14	0.32	303.0	0.6021	−0.1313	26	299	2.09	1.00	483.0	4.1761	−0.3407	17
366	2.14	0.32	293.0	0.6902	−0.2155	26	186	1.07	1.00	458.0	4.1761	0.2053	19
307	2.65	0.60	464.0	0.9494	0.0437	9	271	2.50	0.93	428.5	4.2304	0.3843	30

Table I. (Continued)

$10^{-3}M_W$/(g mol^{-1})	P_d	W_p	T/K	log (μ_0/(Pa·s))	log $\delta\mu_0$	ref	$10^{-3}M_W$/(g mol^{-1})	P_d	W_p	T/K	log (μ_0/(Pa·s))	log $\delta\mu_0$	ref
187	1.19	1.00	453.0	4.2304	0.3798	28	174	1.14	1.00	431.9	5.3802	0.1324	28
271	2.50	1.00	467.5	1.2553	0.1401	30	271	2.50	0.93	400.5	5.3802	0.4764	30
271	2.50	0.76	341.5	4.2788	0.3237	30	271	2.50	1.00	438.5	5.3979	0.3715	7
187	1.19	1.00	453.0	4.2788	0.3314	28	79	1.10	1.00	416.2	5.3979	−0.1307	23
265	2.17	1.00	483.0	4.3010	−0.5962	25	250	2.33	1.00	433.0	5.5441	0.3961	17
271	2.50	0.82	371.5	4.3010	0.4673	30	299	2.09	1.00	443.0	5.5563	0.1192	17
79	1.10	1.00	432.0	4.3222	0.2205	11	271	2.50	0.82	343.0	5.6335	0.2856	30
52	1.12	1.00	423.1	4.3617	0.0805	23	299	2.09	1.00	433.0	5.8751	0.3135	17
193	1.07	1.00	452.0	4.3979	0.2951	28	52	1.12	1.00	404.0	5.8976	−0.5848	23
299	2.09	1.00	473.0	4.4314	−0.1652	17	271	2.50	1.00	429.0	5.9031	0.3568	30
174	1.14	1.00	447.5	4.4314	0.3424	28	271	2.50	0.93	390.5	5.9085	0.4348	30
250	2.33	1.00	463.0	4.4472	0.0552	17	79	1.10	1.00	409.7	5.9445	−0.3631	23
265	2.17	1.00	473.0	4.4771	−0.3484	33	174	1.14	1.00	422.8	6.0414	−0.0727	28
271	2.50	0.93	420.5	4.5051	0.4475	30	111	1.08	1.00	412.0	6.1461	−0.2367	23
261	2.50	1.00	453.0	4.5051	0.5086	12	250	2.33	1.00	423.0	6.2041	0.2607	17
79	1.10	1.00	428.2	4.5682	0.1439	23	271	2.50	0.82	333.0	6.2553	0.1143	30
271	2.50	1.00	457.0	4.6128	0.2599	30	271	2.50	1.00	423.0	6.2788	0.3022	30
259	2.35	1.00	473.0	4.6232	−0.5201	24	271	2.50	0.76	303.0	6.5051	−0.4274	30
299	2.09	1.00	463.0	4.7324	−0.0167	17	299	2.09	1.00	423.0	6.5315	0.1945	17
271	2.50	0.76	331.5	4.7324	0.2203	30	174	1.14	1.00	414.8	6.5441	−0.1579	28
250	2.33	1.00	453.0	4.8062	0.1543	17	271	2.50	1.00	418.5	6.6021	0.2258	30
187	1.19	1.00	438.0	4.8062	0.5027	28	250	2.33	1.00	413.0	6.8513	0.1634	17
187	1.19	1.00	438.0	4.8513	0.4576	28	111	1.08	1.00	402.0	7.1139	−0.6841	23
271	2.50	0.93	410.5	4.8921	0.5015	30	299	2.09	1.00	413.0	7.2304	0.0591	17
174	1.14	1.00	441.8	4.9085	0.1292	11	250	2.33	1.00	403.0	7.7709	−0.1789	17
111	1.08	1.00	431.0	4.9243	0.0629	23	299	2.09	1.00	403.0	8.0792	−0.1983	17
79	1.10	1.00	422.6	4.9638	0.0034	23	193	1.07	1.00	402.0	8.1461	−0.8994	28
271	2.50	1.00	447.5	4.9912	0.3327	30	250	2.33	1.00	393.0	8.7404	−0.5417	17
52	1.12	1.00	414.2	5.0414	−0.2035	23	299	2.09	1.00	393.0	8.9031	−0.4008	17
299	2.09	1.00	453.0	5.1139	0.0711	17	250	2.33	1.00	383.0	9.6435	−0.8065	17
271	2.50	0.82	352.0	5.1461	0.3895	30	299	2.09	1.00	383.0	9.8921	−0.7358	17
250	2.33	1.00	443.0	5.1761	0.2632	17	250	2.33	1.00	373.0	10.5051	−0.9956	30
271	2.50	0.76	322.0	5.2304	0.0752	30	299	2.09	1.00	373.0	10.6990	−0.8537	30

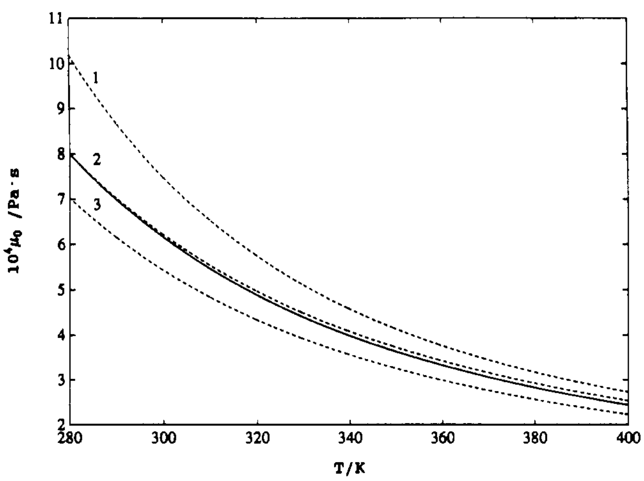

Figure 3. Actual and predicted viscosities of the solvents: —, regression; 1, styrene; 2, toluene; 3, ethylbenzene.

$$\ln(\mu_0/(\text{Pa·s})) = -11.091 + 1109/(T/\text{K}) + M_w^{0.1413}[12.032W_p - 19.501W_p^2 + 2.923W_p^3 + (-1327W_p + 1359W_p^2 + 3597W_p^3)/(T/\text{K})] \quad (3)$$

This correlation is recommended for the ranges $293 \le T/\text{K} \le 513$, $52000 \le M_w \le 380000$, $1 < P_d \le 5$, and $0.05 < W_p \le 1$. The quality of the fit is displayed in Figure 1. Note that the base 10 logarithm is used in Figures 1 and 2 and for the data in Tables I and II. The standard error for the prediction of log μ_0 is 0.307. The Harkness correlation gives a standard error of 0.546 when applied to the same data set.

Correlation with Shear

Table II lists 344 data at shear rates in the range 0.01–28221 s^{-1}. These were correlated by assuming that eq 3 correctly predicted μ_0 and that the difference between μ_0 and the observed value was due to shear. The correlation is

$$\mu = \mu_0/(1 + \mu_0\dot{\gamma}^{1.2}/35000)^{0.60} \quad (4)$$

The quality of the combined fit of eq 4 is displayed in Figure 2. The functional form of eq 4 is a modification of the model used by Hieber and Chiang (*14*). The standard error for prediction of log μ is 0.314 for the data set in Table II.

Conclusions

Equations 3 and 4 are smooth functions that provide reasonable estimates for μ_0 and μ within the range appropriate to industrial polymerizations. The previously used Harkness correlation remains fairly accurate, even for the extended range of data included in this paper. Thus, design studies based on the correlation (*10–13*) are unlikely to contain major errors. However, the present results are a significant improvement and are recommended for future use.

It is hoped that these results will provoke additional experimental measurements. Viscosity correlations for polymers are notoriously inaccurate. The predictions of eq 3 are, on average, only accurate within a factor of 2 in viscosity. Of the 222 data, 8 predictions differ from the experimental results by a factor of 5 or more. One prediction at the extremes of $W_p = 1$ and $T = 513$ K differs by a factor of 15. Additional data are needed, particularly at high temperatures. Polydispersity does not appear in eq 3 and does not significantly affect μ_0. Retaining it in the regression equation generates a factor of $P_d^{-0.01}$ and reduces the standard error in log μ_0 by 0.001.

The deviations between the correlation of eq 3 and the experimental data for μ_0 are shown in Figure 1. The only apparent trend is for larger errors at high viscosities. Note that the experimental results span 12 orders of magnitude, a truly remarkable range for any physical property.

Table II. Data for Apparent Viscosity μ ($\delta\mu$ Is the Ratio of Values Calculated from Equation 4 to Experimental Values)

$10^{-3}M_W$/(g mol^{-1})	P_d	W_p	T/K	log (μ/(Pa·s))	shear/s^{-1}	log $\delta\mu$	ref	$10^{-3}M_W$/(g mol^{-1})	P_d	W_p	T/K	log (μ/(Pa·s))	shear/s^{-1}	log $\delta\mu$	ref
259	2.35	0.50	423.0	0.1903	5800.00	0.1445	25	307	2.65	0.75	503.0	1.0414	354.00	−0.1844	9
259	2.35	0.50	448.0	0.2553	1500.00	0.3262	25	307	2.65	0.75	503.0	1.0414	292.50	−0.1728	9
215	3.18	0.40	473.0	0.2788	8600.00	−0.2884	25	307	2.65	0.60	405.0	1.0792	209.50	0.3270	9
215	3.18	0.60	473.0	0.3010	3700.00	0.0505	25	307	2.65	0.75	493.0	1.7092	457.30	−0.1160	9
259	2.35	0.50	423.0	0.3222	2750.00	0.2032	25	307	2.65	0.75	483.0	1.0792	729.80	−0.0666	9
259	2.35	0.50	448.0	0.3424	750.00	0.3306	25	307	2.65	0.60	424.0	1.0792	168.30	0.1925	9
215	3.18	0.40	473.0	0.3617	4500.00	−0.2264	25	307	2.65	0.75	503.0	1.0792	272.40	−0.2067	9
259	2.35	0.50	448.0	0.3802	1450.00	0.2068	25	307	2.65	0.60	424.0	1.1139	111.20	0.1819	9
259	2.35	0.50	423.0	0.4150	1400.00	0.2493	25	307	2.65	0.60	424.0	1.1139	102.90	0.1855	9
259	2.35	0.50	448.0	0.4232	630.00	0.2662	25	307	2.65	0.60	405.0	1.1139	196.10	0.2998	9
259	2.35	0.50	448.0	0.4314	305.00	0.3044	25	259	2.35	0.70	437.0	1.1139	1500.00	−0.0815	25
215	3.18	0.40	473.0	0.4393	1650.00	−0.1516	25	307	2.65	0.60	424.0	1.1461	64.70	0.1692	9
259	2.35	0.50	423.0	0.4393	1500.00	0.2126	25	307	2.65	0.60	424.0	1.1461	98.00	0.1553	9
215	3.18	0.60	473.0	0.4472	1500.00	0.0758	25	307	2.65	0.60	405.0	1.1461	153.80	0.2918	9
215	3.18	0.40	473.0	0.4472	900.00	−0.1090	25	307	2.65	0.75	503.0	1.1461	172.60	−0.2548	9
215	3.18	0.40	473.0	0.4548	440.00	−0.0848	25	307	2.65	0.60	424.0	1.1461	75.70	0.1647	9
215	3.18	0.40	473.0	0.4624	180.00	−0.0754	25	307	2.65	0.75	503.0	1.1761	69.00	−0.2662	9
259	2.35	0.50	448.0	0.4843	170.00	0.2706	25	307	2.65	0.75	473.0	1.1761	605.70	−0.0213	9
259	2.35	0.50	423.0	0.5051	650.00	0.2672	25	307	2.65	0.75	503.0	1.1761	67.40	−0.2660	9
259	2.35	0.50	448.0	0.5315	250.00	0.2121	25	307	2.65	0.75	493.0	1.1761	279.80	−0.1695	9
259	2.35	0.50	423.0	0.5315	780.00	0.2200	25	307	2.65	0.75	503.0	1.1761	81.30	−0.2683	9
259	2.35	0.50	448.0	0.5315	140.00	0.2274	25	307	2.65	0.60	424.0	1.1761	61.50	0.1406	9
259	2.35	0.50	448.0	0.5502	150.00	0.2074	25	307	2.65	0.60	405.0	1.2041	113.00	0.2581	9
259	2.35	0.50	423.0	0.5798	290.00	0.2543	25	307	2.65	0.60	424.0	1.2041	46.10	0.1187	9
259	2.35	0.50	423.0	0.6021	290.00	0.2320	25	307	2.65	0.60	405.0	1.2304	92.50	0.2443	9
307	2.65	0.60	446.0	0.6021	1198.60	0.2564	9	307	2.65	0.75	493.0	1.2304	195.30	−0.2023	9
259	2.35	0.50	448.0	0.6284	72.00	0.1393	25	307	2.65	0.75	483.0	1.2304	300.00	−0.0953	9
307	2.65	0.60	464.0	0.6335	869.30	0.1861	9	307	2.65	0.75	503.0	1.2304	17.70	−0.3127	9
215	3.18	0.60	473.0	0.6335	370.00	0.0172	25	259	2.35	0.50	423.0	1.2430	22.50	−0.3647	25
307	2.65	0.60	464.0	0.6335	961.50	0.1703	9	307	2.65	0.75	493.0	1.2553	123.20	−0.2089	9
259	2.35	0.50	448.0	0.6767	72.00	0.0910	25	307	2.65	0.60	405.0	1.2553	83.50	0.2248	9
307	2.65	0.60	464.0	0.6812	614.10	0.1856	9	307	2.65	0.75	493.0	1.2553	156.80	−0.2174	9
259	2.35	0.50	423.0	0.6946	155.00	0.1630	25	307	2.65	0.75	493.0	1.2553	107.80	−0.2051	9
259	2.35	0.50	423.0	0.7284	145.00	0.1309	25	259	2.35	0.70	437.0	1.2553	740.00	−0.0428	25
215	3.18	0.60	473.0	0.7324	150.00	−0.0554	25	307	2.65	0.60	405.0	1.2553	49.80	0.2452	9
259	2.35	0.50	423.0	0.7324	125.00	0.1303	25	307	2.65	0.60	405.0	1.2553	73.60	0.2309	9
307	2.65	0.75	503.0	0.7634	1571.90	−0.0954	9	307	2.65	0.75	503.0	1.2553	9.50	−0.3366	9
307	2.65	0.60	464.0	0.7634	401.10	0.1469	9	307	2.65	0.60	405.0	1.2788	93.70	0.1951	9
307	2.65	0.60	405.0	0.7709	917.60	0.3666	9	307	2.65	0.60	405.0	1.2788	53.90	0.2193	9
259	2.35	0.50	423.0	0.7782	70.00	0.0933	25	307	2.65	0.60	405.0	1.2788	47.10	0.2233	9
215	3.18	0.60	473.0	0.7782	74.00	−0.0930	25	307	2.65	0.75	483.0	1.2788	211.40	−0.1140	9
307	2.65	0.60	446.0	0.8062	370.10	0.2330	9	259	2.35	0.50	423.0	1.2900	14.00	−0.4107	25
307	2.65	0.60	446.0	0.8129	331.50	0.2369	9	307	2.65	0.60	405.0	1.3010	37.30	0.2068	9
307	2.65	0.60	464.0	0.8195	249.30	0.1237	9	307	2.65	0.75	473.0	1.3010	344.30	−0.0531	9
259	2.35	0.50	423.0	0.8261	68.50	0.0457	25	307	2.65	0.75	483.0	1.3010	175.00	−0.1236	9
307	2.65	0.60	464.0	0.8451	203.30	0.1081	9	307	2.65	0.60	405.0	1.3010	42.50	0.2038	9
307	2.65	0.75	493.0	0.8633	1424.10	−0.0812	9	307	2.65	0.60	405.0	1.3010	27.60	0.2123	9
307	2.65	0.60	446.0	0.8692	260.10	0.2008	9	307	2.65	0.75	493.0	1.3222	36.30	−0.2553	9
307	2.65	0.60	446.0	0.8692	248.00	0.2043	9	307	2.65	0.75	493.0	1.3222	65.50	−0.2618	9
207	2.65	0.60	424.0	0.8808	562.10	0.2473	9	259	2.35	0.70	448.0	1.3222	775.00	−0.2142	25
307	2.65	0.60	464.0	0.8808	118.80	0.0906	9	307	2.65	0.75	493.0	1.3222	51.40	−0.2586	9
307	2.65	0.60	464.0	0.8921	97.50	0.0838	9	307	2.65	0.75	473.0	1.3617	247.20	−0.0729	9
307	2.65	0.60	446.0	0.8976	185.80	0.1939	9	307	2.65	0.75	473.0	1.3617	252.80	−0.0753	9
307	2.65	0.75	503.0	0.8976	826.70	−0.1241	9	307	2.65	0.75	493.0	1.3617	14.40	−0.2904	9
307	2.65	0.60	464.0	0.9031	83.40	0.0756	9	307	2.65	0.75	483.0	1.3802	80.10	−0.1701	9
307	2.65	0.60	446.0	0.9085	160.40	0.1903	9	186	1.07	1.00	458.0	1.3979	28221.00	−0.1233	9
307	2.65	0.60	464.0	0.9085	67.10	0.0735	9	259	2.35	0.70	437.0	1.4150	300.00	−0.0250	25
307	2.65	0.60	440.0	0.9138	173.10	0.2280	9	307	2.65	0.75	483.0	1.4150	27.70	−0.1882	9
307	2.65	0.60	464.0	0.9138	45.30	0.0723	9	307	2.65	0.75	473.0	1.4150	187.00	−0.0990	9
307	2.65	0.75	483.0	0.9138	1586.00	−0.0656	9	307	2.65	0.75	483.0	1.4150	69.60	−0.2014	9
307	2.65	0.60	446.0	0.9138	151.70	0.1876	9	307	2.65	0.85	484.0	1.4314	428.40	0.0695	9
307	2.65	0.60	405.0	0.9243	464.60	0.3609	9	307	2.65	0.75	473.0	1.4624	129.80	−0.1194	9
307	2.65	0.60	424.0	0.9243	411.40	0.2533	9	307	2.65	0.75	483.0	1.4771	15.70	−0.2470	9
307	2.65	0.60	405.0	0.9345	444.30	0.3590	9	259	2.35	0.70	437.0	1.4771	165.00	−0.0102	25
307	2.65	0.60	446.0	0.9445	112.20	0.1682	9	259	2.35	0.70	448.0	1.4843	310.00	−0.2187	25
307	2.65	0.60	446.0	0.9494	106.20	0.1651	9	307	2.65	0.75	483.0	1.5051	9.10	−0.2734	9
307	2.65	0.60	446.0	0.9685	95.80	0.1489	9	307	2.65	0.85	484.0	1.5185	86.40	0.0715	9
307	2.65	0.75	473.0	0.9823	1430.50	−0.0211	9	307	2.65	0.75	473.0	1.5185	86.40	−0.1548	9
307	2.65	0.60	424.0	0.9912	293.70	0.2297	9	307	2.65	0.85	484.0	1.5315	244.20	0.0888	9
307	2.65	0.75	493.0	0.9912	772.90	−0.0969	9	259	2.35	0.70	437.0	1.5378	83.00	−0.0180	25
307	2.65	0.75	503.0	0.9912	491.00	−0.1597	9	307	2.65	0.85	473.0	1.5563	34.98	0.5203	9
307	2.65	0.60	446.0	1.0000	40.90	0.1322	9	307	2.65	0.75	473.0	1.5682	43.50	−0.1845	9
307	2.65	0.60	424.0	1.0000	251.00	0.2377	9	259	2.35	0.70	448.0	1.5911	155.00	−0.2559	25
307	2.65	0.60	446.0	1.000	56.40	0.1282	9	307	2.65	0.75	473.0	1.6021	24.10	−0.2101	9
307	2.65	0.60	446.0	1.0000	33.20	0.1341	9	307	2.65	0.75	473.0	1.6128	10.90	−0.2156	9
307	2.65	0.60	405.0	1.0414	281.80	0.3267	9	307	2.65	0.85	473.0	1.6128	23.73	0.4860	9
307	2.65	0.60	424.0	1.0414	219.70	0.2090	9	259	2.35	0.70	437.0	1.6335	33.50	−0.0814	25

Table II. (Continued)

$10^{-3}M_W$/(g mol^{-1})	P_d	W_p	T/K	log (μ/(Pa·s))	shear/s^{-1}	log $\delta\mu$	ref	$10^{-3}M_W$/(g mol^{-1})	P_d	W_p	T/K	log (μ/(Pa·s))	shear/s^{-1}	log $\delta\mu$	ref
259	2.35	0.70	423.0	1.6435	300.00	−0.1063	25	307	2.65	1.00	493.0	2.6721	49.90	0.1829	9
259	2.35	0.70	448.0	1.6484	77.00	−0.2757	25	259	2.35	0.90	473.0	2.7033	86.00	−0.4530	25
186	1.07	1.00	458.0	1.6532	13154.00	−0.1399	19	307	2.65	1.00	493.0	2.7076	39.00	0.2154	9
307	2.65	0.85	484.0	1.6628	133.10	0.0551	9	307	2.65	1.00	474.0	2.7160	99.60	0.2703	9
307	2.65	0.85	484.0	1.6902	103.60	0.0580	9	307	2.65	1.00	493.0	2.7160	40.10	0.1995	9
259	2.35	0.70	448.0	1.7160	32.50	−0.3228	25	265	2.17	1.00	473.0	2.7482	260.00	−0.1099	33
307	2.65	0.85	484.0	1.7160	97.80	0.0384	9	307	2.65	1.00	493.0	2.7482	46.80	0.1247	9
259	2.35	0.70	423.0	1.7482	155.00	−0.1020	25	259	2.35	0.90	498.0	2.7853	35.00	-1.0020	25
259	2.35	0.70	448.0	1.7482	20.00	−0.3497	25	259	2.35	0.90	423.0	2.7993	160.00	0.0442	25
307	2.65	0.85	473.0	1.7482	12.39	0.3727	9	259	2.35	0.90	473.0	2.8162	42.00	−0.4367	25
259	2.35	0.70	448.0	1.7482	16.00	−0.3481	25	259	2.35	0.90	498.0	2.8195	16.50	-1.0174	25
307	2.65	0.85	484.0	1.7709	70.10	0.0142	9	307	2.65	1.00	493.0	1.8161	23.10	0.2320	9
259	2.35	0.70	437.0	1.8062	15.00	−0.2430	25	259	2.35	1.00	473.0	2.8325	205.00	−0.1305	25
259	2.35	0.70	448.0	1.8261	6.60	−0.4226	25	307	2.65	1.00	474.0	2.8513	62.80	0.2777	9
307	2.65	0.85	473.0	1.8513	87.10	0.1308	9	259	2.35	0.90	448.0	2.8513	80.00	−0.1727	25
307	2.65	0.85	473.0	1.8573	75.80	0.1438	9	307	2.65	1.00	493.0	2.8513	18.30	0.2615	9
259	2.35	0.70	448.0	1.8633	8.10	−0.4603	25	259	2.35	0.90	498.0	2.8513	20.00	-1.0526	25
307	2.65	0.85	484.0	1.8692	30.50	−0.0385	9	259	2.35	0.90	498.0	2.8692	8.00	-1.0592	25
259	2.35	0.70	423.0	1.8751	75.00	−0.1540	25	259	2.35	0.90	473.0	2.8808	32.00	−0.4647	25
307	2.65	0.85	484.0	1.8921	32.00	−0.0632	9	259	2.35	0.90	498.0	2.8865	7.10	-1.0757	25
307	2.65	0.85	473.0	1.9085	60.20	0.1202	9	307	2.65	1.00	493.0	2.9191	11.80	0.2853	9
186	1.07	1.00	458.0	1.9191	6191.00	−0.1702	19	259	2.35	0.90	498.0	2.9345	2.90	-1.1204	25
259	2.35	0.70	423.0	1.9243	34.00	−0.1618	25	186	1.07	1.00	458.0	2.9445	202.80	−0.1272	19
307	2.65	0.85	484.0	1.9243	13.00	−0.0743	9	259	2.35	0.90	498.0	2.9445	1.30	-1.1293	25
259	2.35	0.70	423.0	1.9542	21.50	−0.1794	25	259	2.35	0.90	423.0	2.9823	86.00	0.0541	25
259	2.35	0.70	423.0	1.9542	19.50	−0.1775	25	307	2.65	1.00	474.0	2.9868	33.70	0.3330	9
307	2.65	0.85	484.0	1.9638	9.90	−0.1107	9	307	2.65	1.00	493.0	3.0000	7.10	0.2891	9
259	2.35	0.70	437.0	1.9777	7.75	−0.4107	25	259	2.35	0.90	473.0	3.0212	21.70	−0.5641	25
259	2.35	0.70	423.0	1.9777	16.50	−0.1982	25	259	2.35	0.90	423.0	3.0212	82.00	0.0299	25
259	2.35	0.70	423.0	1.9823	22.50	−0.2085	25	307	2.65	1.00	493.0	3.0414	6.10	0.2684	9
307	2.65	1.00	513.0	1.9956	383.60	−0.0777	9	265	2.17	1.00	473.0	3.0414	117.00	−0.1548	33
259	2.35	0.70	448.0	2.0212	2.30	−0.6164	25	259	2.35	1.00	473.0	3.0607	105.00	−0.1510	25
259	2.35	0.70	423.0	2.0414	9.60	−0.2558	25	259	2.35	0.90	473.0	3.0607	16.50	−0.5817	25
259	2.35	0.70	423.0	2.0531	7.20	−0.2655	25	259	2.35	0.90	448.0	3.1038	31.00	−0.1669	25
259	2.35	0.70	423.0	2.0607	2.80	−0.2698	25	307	2.65	1.00	474.0	3.1139	15.40	0.4396	9
307	2.65	1.00	513.0	2.1139	245.90	−0.0671	9	259	2.35	0.90	473.0	3.1614	7.30	−0.6431	25
307	2.65	1.00	493.0	2.1139	393.40	0.1211	9	265	2.17	1.00	513.0	3.1761	16.30	−0.7075	33
307	2.65	0.85	473.0	2.1139	28.40	−0.0243	9	186	1.07	1.00	458.0	3.1761	98.24	−0.1331	19
307	2.65	0.85	473.0	2.1461	18.80	−0.0376	9	265	2.17	1.00	483.0	3.1761	49.60	−0.2046	25
307	2.65	0.85	473.0	2.1761	8.80	−0.0485	9	259	2.35	0.90	448.0	3.1903	22.50	−0.1765	25
265	2.17	1.00	473.0	2.2041	1300.00	−0.0683	33	265	2.17	1.00	493.0	3.2041	19.60	−0.1937	33
307	2.65	0.85	473.0	2.2041	4.30	−0.0687	9	259	2.35	0.90	473.0	3.2175	2.70	−0.6807	25
259	2.35	0.70	423.0	2.2041	1.10	−0.4121	25	259	2.35	0.90	423.0	3.2672	34.00	0.0546	25
186	1.07	1.00	458.0	2.2041	2312.00	−0.1472	29	259	2.35	1.00	473.0	3.2672	55.00	−0.1584	25
259	2.35	0.90	498.0	2.2304	310.00	−0.6852	25	265	2.17	1.00	473.0	3.2788	55.60	−0.1627	33
307	2.65	1.00	493.0	2.2304	262.70	0.1294	9	259	2.35	0.90	448.0	3.2856	17.00	−0.2108	25
307	2.65	1.00	513.0	2.2304	151.80	−0.0510	9	265	2.17	1.00	513.0	3.3010	8.17	−0.7984	33
259	2.35	1.00	473.0	2.3010	1050.00	−0.1088	25	307	2.65	1.00	474.0	3.3222	6.20	0.4826	9
307	2.65	1.00	513.0	2.3222	99.00	−0.0347	9	265	2.17	1.00	493.0	3.3617	9.44	−0.2224	33
307	2.65	1.00	513.0	2.3424	87.20	−0.0250	9	259	2.35	0.90	398.0	3.3617	78.00	0.1155	25
307	2.65	1.00	493.0	2.3617	150.90	0.1677	9	259	2.35	1.00	473.0	3.3802	33.80	−0.1237	25
307	2.65	1.00	513.0	2.3979	61.80	−0.0055	9	265	2.17	1.00	513.0	3.3979	3.27	−0.8758	33
307	2.65	1.00	513.0	2.4150	56.50	−0.0047	9	259	2.35	0.90	448.0	3.4150	9.00	−0.2270	25
307	2.65	1.00	513.0	2.4150	66.00	−0.0362	9	186	1.07	1.00	458.0	3.4150	47.74	-0.1484	33
307	2.65	1.00	513.0	2.4314	50.30	0.0011	9	265	2.17	1.00	483.0	3.4472	20.40	−0.2260	25
259	2.35	0.90	498.0	2.4314	160.00	−0.7724	25	265	2.17	1.00	513.0	3.4472	1.63	−0.9193	33
307	2.65	1.00	513.0	2.4314	45.00	0.0212	9	259	2.35	0.90	388.0	3.4771	68.00	0.2212	25
186	1.07	1.00	458.0	2.4314	1106.00	−0.1440	19	259	2.35	0.90	448.0	3.4771	6.95	−0.2537	25
259	2.35	0.90	448.0	2.4393	310.00	−0.1683	25	259	2.35	0.90	423.0	3.5051	16.50	0.0332	25
307	2.65	1.00	513.0	2.4624	37.30	0.0215	9	265	2.17	1.00	473.0	3.5315	20.80	−0.1198	33
307	2.65	1.00	493.0	2.5051	100.00	0.1481	9	265	2.17	1.00	493.0	3.5315	3.48	−0.2922	33
265	2.17	1.00	473.0	2.5185	520.00	−0.0965	33	259	2.35	1.00	473.0	3.5315	22.50	−0.1540	25
307	2.65	1.00	513.0	2.5315	22.90	0.0185	9	265	2.17	1.00	513.0	3.5441	0.82	-1.0137	33
259	2.35	0.90	473.0	2.5378	155.00	−0.4252	25	259	2.35	1.00	473.0	3.5798	18.50	−0.1453	25
259	2.35	1.00	473.0	2.5441	550.00	−0.1499	25	259	1.35	0.90	423.0	3.6021	9.80	0.0854	25
259	2.35	0.90	423.0	2.5682	340.00	0.0402	25	259	2.35	0.90	398.0	3.6335	33.00	0.1123	25
307	2.65	1.00	493.0	2.5798	73.40	0.1646	9	259	2.35	0.90	448.0	3.6435	2.00	−0.3236	25
259	2.35	0.90	498.0	2.5798	80.00	−0.8439	25	265	2.17	1.00	483.0	3.6435	9.58	−0.2401	25
259	2.35	0.90	498.0	2.5798	84.00	−0.8481	25	265	2.17	1.00	513.0	3.6532	0.33	-1.1215	33
307	2.65	1.00	513.0	2.5911	17.10	−0.0116	9	259	2.35	0.90	423.0	3.6990	7.70	0.0545	25
307	2.65	1.00	513.0	2.5911	13.70	0.0065	9	259	2.35	0.90	388.0	2.6990	33.00	0.2252	25
307	2.65	1.00	474.0	2.6128	136.70	0.2751	9	265	2.17	1.00	493.0	3.7076	1.66	−0.4353	33
307	2.65	1.00	493.0	2.6335	55.60	0.1909	9	259	2.35	1.00	473.0	3.7243	11.50	−0.1561	25
307	2.65	1.00	513.0	2.6335	7.00	0.0003	9	186	1.07	1.00	458.0	3.7404	18.46	−0.1843	19
186	1.07	1.00	458.0	2.6435	531.10	−0.1268	19	265	2.17	1.00	473.0	3.7482	9.58	−0.1184	33
259	2.35	0.90	448.0	2.6435	160.00	−0.1705	25	259	2.35	1.00	473.0	3.7634	10.00	−0.1576	25
307	2.65	1.00	493.0	2.6628	50.70	0.1877	9	265	2.17	1.00	493.0	3.8129	0.82	−0.5361	33

Table II. (Continued)

$10^{-3}M_W$/(g mol^{-1})	P_d	W_p	T/K	log (μ/(Pa·s))	shear/s^{-1}	log $\delta\mu$	ref	$10^{-3}M_W$/(g mol^{-1})	P_d	W_p	T/K	log (μ/(Pa·s))	shear/s^{-1}	log $\delta\mu$	ref
259	2.35	1.00	473.0	3.8293	7.75	−0.1572	25	265	2.17	1.00	473.0	4.1461	1.69	−0.1589	33
259	2.35	0.90	388.0	3.8692	18.00	0.2443	25	265	2.17	1.00	483.0	4.2041	0.30	−0.5080	25
265	2.17	1.00	483.0	3.8808	3.45	−0.3049	25	265	2.17	1.00	473.0	4.2553	0.81	−0.1946	33
259	2.35	0.90	398.0	3.8808	15.50	0.1002	25	265	2.17	1.00	473.0	4.3617	0.30	−0.2556	33
265	2.17	1.00	493.0	3.9191	0.31	−0.6245	33	259	2.35	1.00	473.0	4.4472	0.33	−0.3684	25
259	2.35	0.90	388.0	3.9294	15.50	0.2308	25	259	2.35	0.90	398.0	4.4843	2.25	0.0846	25
186	1.07	1.00	458.0	3.9294	9.02	−0.1639	19	259	2.35	1.00	473.0	4.5119	0.21	−0.4229	25
259	2.35	1.00	473.0	3.9345	5.00	−0.1578	25	259	2.35	1.00	473.0	4.5185	0.13	−0.4231	25
259	2.35	1.00	473.0	3.9731	4.15	−0.1561	25	259	2.35	1.00	473.0	4.5378	0.08	−0.4396	25
265	2.17	1.00	483.0	4.000	1.63	−0.3554	25	259	2.35	1.00	473.0	4.5682	0.05	−0.4679	25
259	2.35	0.90	423.0	4.000	2.90	−0.0126	25	259	2.35	1.00	473.0	4.6021	0.01	−0.4996	25
186	1.07	1.00	458.0	4.0414	4.41	−0.0835	19	259	2.35	1.00	473.0	4.6128	0.03	−0.5113	25
259	2.35	0.90	398.0	4.0607	8.60	0.1027	25	259	2.35	1.00	473.0	4.6232	0.02	−0.5211	25
259	2.35	0.90	388.0	4.0969	9.00	0.2327	25	259	2.35	1.00	473.0	4.6232	0.01	−0.5204	25
259	2.35	0.90	423.0	4.0969	1.40	0.0151	25	259	2.35	0.90	388.0	4.6435	1.75	0.1908	25
265	2.17	1.00	483.0	4.1139	0.80	−0.4364	25	259	2.35	1.00	473.0	4.6532	0.01	−0.5507	25
186	1.07	1.00	458.0	4.1139	1.72	0.0484	19	259	2.35	0.90	398.0	4.6990	1.00	0.0972	25
259	2.35	1.00	473.0	4.1303	2.00	0.1850	25	259	2.35	0.90	388.0	4.9731	0.61	0.1701	25

The correlation for the shear-sensitive viscosity is nearly as accurate as that for μ_0. The scatter diagram in Figure 2 does, however, suggest some systematic errors between the correlation and some data set. Of the 344 data with $\dot{\gamma} > 0$, 16 predictions differ by a factor of 5 or more.

The data in Table I are pooled for three separate solvents: toluene, ethylbenzene, and styrene. These are all good solvents for polystyrene and have fairly similar viscosities as shown in Figure 3. The first two terms in eq 3, $-11.091 + 1109/T$, correspond to a hypothetical fluid which has a viscosity within the range of the three real solvents. For process engineering purposes, the suggested correlation thus appears reasonable for dilute solutions, although the lower experimental limit on W_p is 0.06.

Glossary

M_w	weight-average molecular weight
P_d	polydispersity
T	temperature (K)
W_p	weight fraction of polymer

Greek Letters

μ	apparent viscosity (Pa·s)
μ_0	zero shear viscosity (Pa·s)
$\dot{\gamma}$	shear rate (s^{-1})
σ	standard error

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Received for review November 12, 1991. Revised April 21, 1992. Accepted May 26, 1992.

Registry No. PS (homopolymer), 9003-53-6.