Viscoelastic Properties of Polyisobutylene Melts

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ABSTRACT: The viscoelastic response of polyisobutylene melts in the terminal and plateau zones was studied for a wide range of molecular weights ($2.7 \times 10^4 \leq M \leq 1.6 \times 10^6$) and temperatures (−30 °C ≤ T ≤ +220 °C). Results are reported for whole polymers and fractions of both commercial and laboratory materials. Storage and loss moduli were recorded for a wide range of frequencies ($10^{-3}\ \mathrm{s}^{-1} \leq \omega \leq 10^2\ \mathrm{s}^{-1}$) at each temperature and shifted to form master curves by the usual superposition procedures. The shift in modulus scale with temperature was similar for all samples and in accord with predictions based on the temperature dependence of density and chain dimensions for polyisobutylene. For laboratory samples, the shift in frequency scale obeyed the WLF equation, although with WLF coefficients that differ somewhat from earlier results. The frequency shift in commercial materials, whether fractionated or not, behaved in a more complicated fashion. Different WLF equations were required to describe the low- and high-temperature ranges. The effects of molecular weight and distribution were unexceptional, however, and consistent with results for other species of linear polymers.

Introduction

The preceding paper deals with the dilute-solution properties of polyisobutylene.[1] Here we use many of the same samples to investigate its viscoelastic properties in the melt state. Fox and Flory established a relationship between melt viscosity and molecular weight for polyisobutylene,[2,3] but the more detailed studies of its viscoelastic response have focused primarily on the behavior of individual samples.[4,5] The present work explores linear response, mainly in the plateau and terminal zones, for molecular weights ranging from 2.7×10^4 to 1.6×10^6 and a considerably wider temperature range, −30 to +220 °C, than in the earlier studies.

Experimental Section

1. **Samples.** A total of 18 samples was used. Their molecular weights and polydispersities, obtained as described in the previous paper,[1] are listed in Table I. The samples are designated L, PS, or C according to source and manner of preparation. The L and PS samples were synthesized in laboratory reactors, the L samples being obtained from Dr. H.-C. Wang of the Exxon Chemical Co. and the PS samples from Polyscience, Inc. The C samples are commercial reactor products. All samples except 18L, 12L, 16L, and 18C have relatively narrow molecular weight distributions.

Table I
Molecular Characteristics of Polyisobutylene Samples

sample	$\bar{M}_w{}^a \times 10^{-5}$	$\bar{M}_z/\bar{M}_w{}^b$	$\bar{M}_w/\bar{M}_n{}^b$	$[\eta]$,^{c} dL g^{-1}
2PS	0.27	1.09	1.10	0.276
3C	0.64	1.12	1.14	0.480
5PS	1.08	1.16	1.21	0.722
6C	1.27	1.14	1.15	0.778
7C	1.29	1.16	1.13	0.811
8PS	1.33	1.05	1.11	0.847
9C	1.67	1.13	1.21	1.02
10L	2.21	1.84	1.93	1.16
11L	3.25	1.38	1.37	1.63
12C	3.30	1.25	1.31	1.68
13L	3.30	1.92	1.96	1.68
14L	4.36	1.40	1.44	1.98
15C	4.48	1.51	1.46	2.07
16L	6.32	1.91	1.98	2.54
17C	7.45	1.27	1.30	2.97
18C	10.1	2.04	2.28	3.75
19C	14.8	1.24	1.24	4.82
20C	16.1	1.52	1.53	5.33

[a] Obtained by low-angle laser light scattering.[1] [b] Obtained by size-exclusion chromatography (THF, 25 °C), not corrected for axial dispersion.[1] [c] Obtained in cyclohexane at 25 °C.[1]

2. **Rheological Measurements.** Dynamic and storage shear moduli, $G'(\omega)$ and $G''(\omega)$, were determined with a Rheometrics System IV rheometer using the dynamic head, a 10 000 cm g transducer, and parallel plates each with a 25-mm diameter. Sample thicknesses ranged from 1.0 to 1.8 mm. Measurements were made on thoroughly dried samples over a wide range of temperatures, typically from −30 to +200 °C at ~25 °C intervals. The sample chamber was purged continuously with a high-purity nitrogen gas supply for temperatures above 25 °C and with a liquid nitrogen supply at the lower temperatures. Temperature was read with a digital thermometer (Fluke 2190A) just touching the side of the sample and also monitored throughout the runs by a thermocouple located in the center of the upper plate. The latter readings were typically 1–2° higher for runs above ambient and 2–3 °C lower for runs at the lower temperatures. The digital thermometer values are reported here and used in all subsequent calculations.

Measurements commenced at a frequency of $\omega = 4 \times 10^2\ \mathrm{s}^{-1}$, which was then decreased at regular intervals down to $\omega = 1 \times 10^{-3}\ \mathrm{s}^{-1}$ or until the torque amplitude became too small to be measured reliably (<20 cm g). The strain amplitude was increased as necessary to maintain the torque above 20 cm g. Linearity of response was tested whenever the strain amplitude was changed; all data reported here were obtained in the linear range. Strain values ranged from 2% in regions of high modulus to 100% for the lowest moduli. Some experiments were conducted with 8-mm plates to minimize instrumental compliance effects in the high-modulus region. Whenever possible, zero-shear viscosities were obtained from the limiting behavior of loss modulus at low frequencies:[6]

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{1}$$

Values of η_0 so obtained are given in Table II.

Dynamic moduli obtained at different temperatures were combined to form a master curve for each sample. A reference temperature T_0 of 25 °C was used in all cases. According to the time–temperature superposition principle[6]

$$G'(\omega;T) = G'(a_T\omega;T_0)/b_T \tag{2}$$

$$G''(\omega;T) = G''(a_T\omega;T_0)/b_T \tag{3}$$

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Table II
Melt Viscosity (Poise) of Polyisobutylene Samples

sample	25 °C	50 °C	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C	220 °C
2PS[a]	9.59×10^4	1.50×10^4	2.93×10^3	7.46×10^2	2.67×10^2	1.18×10^2	5.70×10^1		
3C	1.61×10^6		4.91×10^4	9.83×10^3		1.17×10^3	4.80×10^2		
5PS	8.80×10^6	1.53×10^6	3.47×10^5	1.01×10^3	3.83×10^4	1.49×10^4	6.65×10^3	2.92×10^3	
6C	1.11×10^7	1.61×10^6	3.57×10^5	9.26×10^4	2.92×10^4	1.03×10^4	3.72×10^3	1.35×10^3	
7C	1.76×10^7	2.53×10^6	5.18×10^5	1.38×10^5	4.37×10^4	1.05×10^4	4.53×10^3	1.76×10^3	
8PS	1.39×10^7	2.19×10^6	4.63×10^5	1.42×10^5	5.74×10^4	2.37×10^4	1.03×10^4	3.33×10^3	
9C	4.42×10^7		1.58×10^6	4.38×10^5		4.62×10^4	1.91×10^4	7.03×10^3	
10L	9.44×10^7		3.13×10^6	8.66×10^5	3.34×10^5	1.28×10^5	5.44×10^4	2.73×10^4	
11L	3.80×10^8		1.33×10^7	3.80×10^6	1.47×10^6	6.11×10^5	2.62×10^5	1.43×10^5	
12C	3.98×10^8		1.37×10^7	4.02×10^6		5.16×10^5	1.81×10^5	8.25×10^4	
13L	4.27×10^8		1.59×10^7	4.79×10^6	1.95×10^6	8.32×10^5	3.78×10^5	1.95×10^5	
14L				9.60×10^6	3.64×10^6	1.67×10^6	8.21×10^5	4.10×10^5	
15C				1.21×10^7		1.64×10^6	7.81×10^5	4.23×10^5	
16L						5.31×10^6	2.49×10^6	1.23×10^6	
17C						8.86×10^6	4.54×10^6	2.43×10^6	1.48×10^6
18C						2.63×10^7	1.18×10^7	6.20×10^6	
19C						6.20×10^7	2.90×10^7	1.63×10^7	9.35×10^6
20C							3.41×10^7 [b]		1.50×10^7

[a] Values at 0 and −15 °C are 1.08×10^6 and 7.39×10^6 P, respectively. [b] Value measured at 185 °C.

Table III
Average and Standard Deviation of the Modulus Scale Shift Factor

T, °C	b_T	std dev	T, °C	b_T	std dev
−30	1.12	0.08	100	0.97	0.12
−15	1.09	0.08	125	0.88	0.07
0	1.05	0.03	150	0.92	0.15
25	1.00		175	0.91	0.11
50	0.97	0.05	200	0.91	0.14
75	0.94	0.05	220	0.88	0.11

where a_T and b_T are empirically determined shift factors relating the responses at temperatures T and T_0 ($a_T = 1$ and $b_T = 1$ at T_0). Superposition was quite satisfactory in all cases. The master curves for four samples, representing a wide range of average molecular weights, are shown in Figures 1–4. They are in fact quite typical of the results for flexible-chain polymer melts, ranging from slightly entangled to highly entangled, and with shapes in the low-frequency range (plateau and terminal regions) that are influenced by molecular weight distribution.[6]

When time–temperature superposition is applicable, the melt viscosity of the sample changes with temperature in a manner that depends only on the shift factors:[6]

$$\eta_0(T) = (a_T/b_T)\eta_0(T_0) \tag{4}$$

For melts of linear polymers in the high molecular weight range ($M_n > 10^4$ in most cases), a_T and b_T are insensitive to both molecular weight and molecular weight distribution, and b_T depends only weakly on the temperature. The modulus shifts are indeed small for polyisobutylene. The averages of values obtained for b_T are listed in Table III. The values of a_T differ among the samples, which will be discussed later.

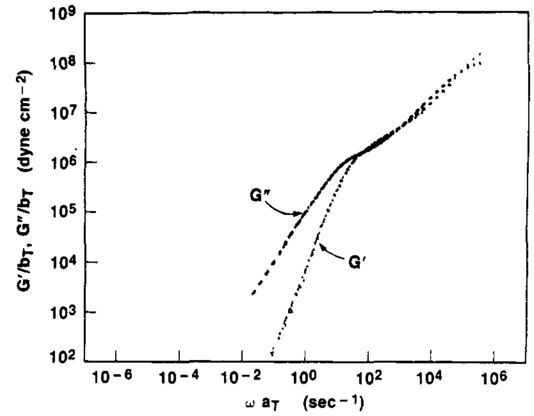

Figure 1. Dynamic moduli master curve for sample 2PS. Reference temperature T_0 is 25 °C.

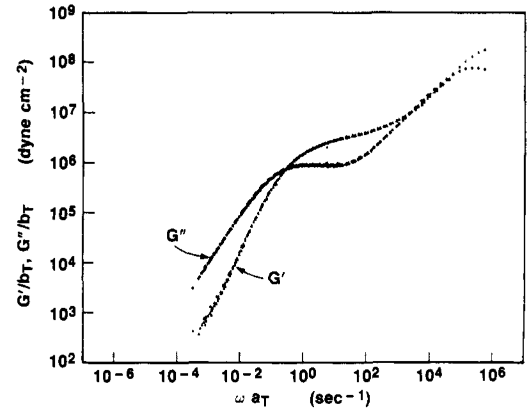

Figure 2. Dynamic moduli master curve for sample 6C. Reference temperature T_0 is 25 °C.

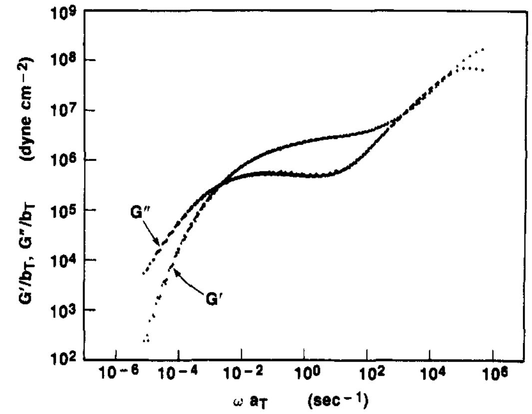

Figure 3. Dynamic moduli master curve for sample 13L. Reference temperature T_0 is 25 °C.

The compliance of the instrument begins to influence the results obtained with 25-mm plates for moduli greater than $\sim 10^7$ dyn/cm^2. Thus, the moduli in the high-frequency range (the transition region, $a_T\omega \geq 10^3$ s^{-1} in this case) are inaccurate. Value of $G''(\omega)$ obtained with 8-mm plates, for which the compliance effect is smaller, are compared with the 25-mm plate results in Figure 5 (sample 19C, $T = -30$ °C). Both $G'(\omega)$ and $G''(\omega)$ appear to obey a power law in the transition region, $G'(\omega)$ and $G''(\omega) \propto \omega^\alpha$ with $\alpha \sim 0.6$, up to at least 10^8 dyn/cm^2. Behavior in this region is insensitive to molecular weight and distribution, as is the case for many other polymer species.[6]

The plateau modulus of polyisobutylene was determined from the area under the terminal loss peak:[6]

$$G_N^\circ = \frac{2}{\pi}\int_{-\infty}^{\infty} G''(\omega)\, \mathrm{d} \ln \omega \tag{5}$$

Data at 75 and 220 °C for sample 20C, the sample of highest

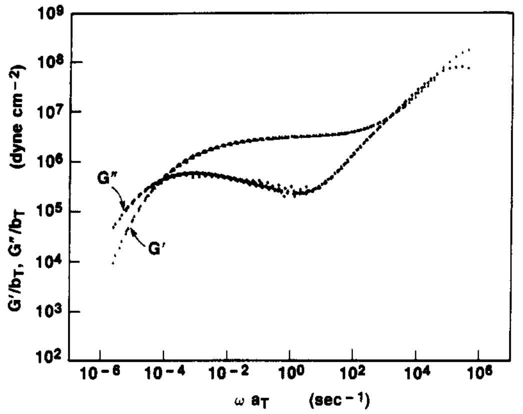

Figure 4. Dynamic moduli master curve for sample 18C. Reference temperature T_0 is 25 °C.

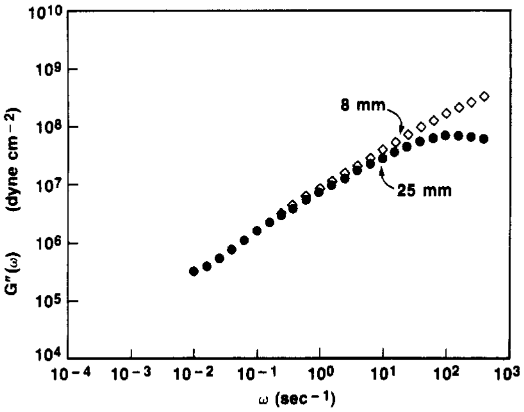

Figure 5. Loss modulus vs frequency for sample 19C at −30 °C as obtained with plates of different diameter.

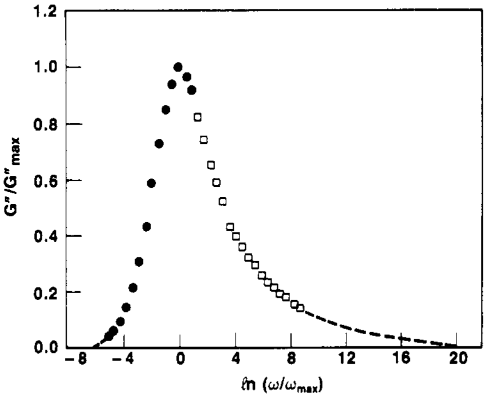

Figure 6. Reduced loss modulus–frequency plot for sample 20C. Data at 75 (□) and 220 °C (●) were used. The area under this curve is related to the plateau modulus (see eq 5).

molecular weight, were superposed (Figure 6), and the relatively minor contribution from the transition region was eliminated by a simple extrapolation procedure. The value obtained, $G_N° = 3.18 \times 10^6$ dyn/cm^2, is in fairly good agreement with the reported result of 2.9×10^6 dyn/cm^2 for polyisobutylene.[6]

Results

1. Modulus–Temperature Shift Factor. The average values of b_T (Table III) are plotted as a function of temperature in Figure 7 along with the predictions of two theories:[6,7]

$$b_T = (\rho T)_0/\rho T \qquad (6)$$

$$b_T = (\rho^2 T C_\infty)_0/\rho^2 T C_\infty \qquad (7)$$

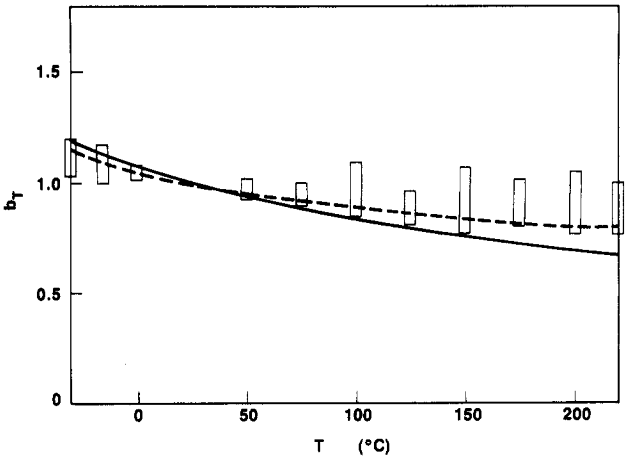

Figure 7. Composite of results for the modulus scale shift factor as a function of temperature. The solid line was calculated with eq 6 and the dashed line with eq 7.

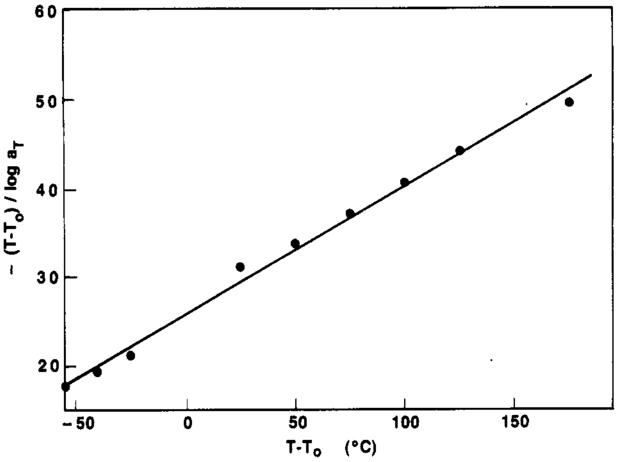

Figure 8. WLF plot for sample 8PS.

The temperature dependences of melt density ρ and characteristic ratio C_∞ for PIB were calculated from refs 1, 3, and 8.

$$\rho = [1.077 + 6.8 \times 10^{-4}(T - 273)]^{-1}\ (\mathrm{g\ cm^{-3}}) \qquad (8)$$

$$C_\infty = 6.8 \text{ at } 25\ ^\circ\mathrm{C} \qquad (9)$$

$$\frac{\mathrm{d}\ln C_\infty}{\mathrm{d}T} = -0.2 \times 10^{-3}\ (\mathrm{K^{-1}}) \qquad (10)$$

Values of b_T calculated with eq 7 are within the error bars over the entire range; the prediction of eq 6 is less satisfactory. However, b_T in any case is very insensitive to temperature, and the values obtained for a_T (see below) are not changed in any significant way if eq 6, eq 7, or even $b_T = 1$ is used at all temperatures.

2. Time–Temperature Shift Factor. The values of a_T were analyzed with the WLF equation:[6]

$$-\log a_T = \frac{C_1(T - T_0)}{C_2 = T - T_0} \qquad (11)$$

For high molecular weight melts, the WLF coefficients C_1 and C_2 are expected to depend only on polymer species and the choice of reference temperature. The results are consistent with eq 11 for some samples (see Figures 8 and 9) but not for others (Figure 10 and 11). Furthermore, with only one exception (sample 5PS), all laboratory reactor products (the L and PS series) behaved in a

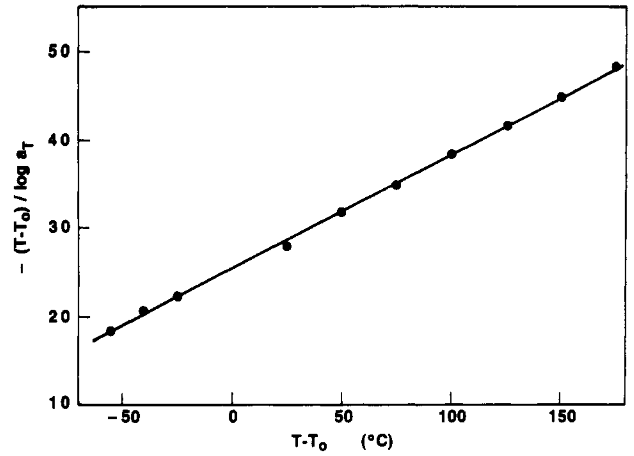

Figure 9. WLF plot for sample 16L.

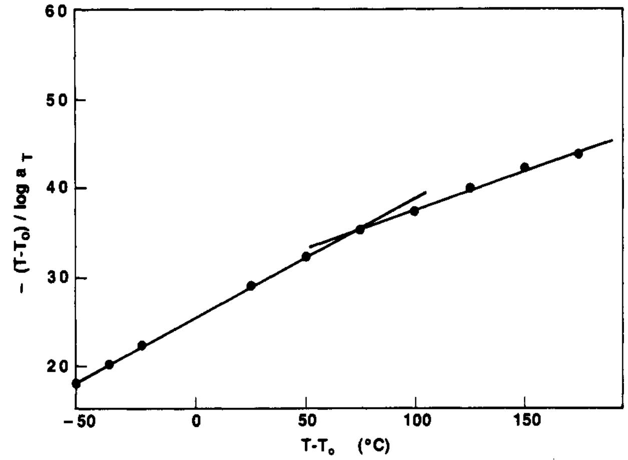

Figure 10. WLF plot for sample 6C.

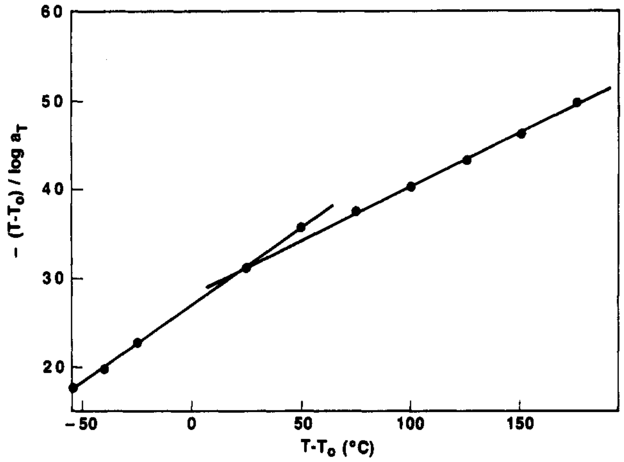

Figure 11. WLF plot for sample 18C.

conventional fashion, while the commercial reactor products (the C series) always gave the curious "segmented" behavior shown in Figures 10 and 11. The temperature at the break is not the same for all samples; T_b ranges from 50 to 150 °C with no apparent pattern. The WLF coefficients obtained for the conventionally behaved samples are listed in Table IV. The data on all those samples agreed within experimental error, giving

$$-\log a_T = \frac{7.49(T - T_0)}{192 + T - T_0} \qquad (12)$$

for the average of all data from −30 to +200 °C. The WLF coefficients differ somewhat from published values,[6] C_1 = 8.61 and C_2 = 200 K for T_0 = 25 °C, which had been obtained from data over a somewhat lower and narrower range of temperatures.

Table IV
WLF Coefficients for Conventionally Behaved Samples of Polyisobutylene

sample	$M_w \times 10^{-5}$	C_1	C_2, K
2PS	0.27	7.88	202
8PS	1.33	6.92	180
10L	2.21	7.63	197
11L	3.25	7.49	190
13L	3.40	7.49	190
14L	4.36	7.32	189
16L	6.32	7.70	196

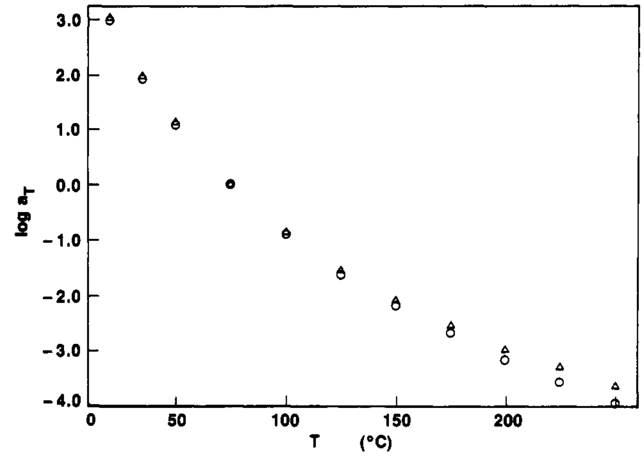

Figure 12. Time-scale shift factor as a function of temperature. Symbols represent data for sample 7C (○) and sample 10L (△).

Figure 12 compares a_T vs T for a commercial sample and a laboratory sample directly. Although the difference is not large, especially considering the wide range of temperatures involved, it is clear that a_T changes more rapidly at high temperatures for the commercial sample. We could find no evidence from IR and ^{13}C NMR of differences in chemical microstructure between the commercial and laboratory products, however, and no evidence from size-exclusion chromatography of differences caused by chain degradation.

Data from the earlier polyisobutylene literature[3-5] also suggest departures from conventional WLF behavior for commercial samples. Fox and Flory report melt viscosities for two polyisobutylene fractions (M = 80 000 and 480 000) over a wide temperature range.[3] (From comments in ref 2 we assume these were the products of commercial reactors.) Those data were converted to a_T values using eq 4; the results are shown in Figure 13. Also shown there are a_T values obtained from dynamic compliance measurements by Ferry and co-workers[4] and from stress relaxation measurements by Tobolsky and co-workers[5] on the NBS standard polyisobutylene (almost certainly a commercial reactor product). The solid lines in Figure 13 represent the results obtained here for the commercial product 18C and the laboratory product 16L. The values of a_T from melt viscosity[3] cover the range above room temperature and agree quite well with the 18C results in that range. Values from the dynamic measurements[4,5] cover mainly lower temperatures, and below ~ −35 °C they merge nicely with the extrapolated line for 18C. However, they begin to depart from the 18C results above $T - T_0 = -60$ °C ($T = -35$ °C) and follow a different course at higher temperatures. The latter behavior resembles the "two-WLF" segmented form found here for commercial reactor products but with the break near −35 °C instead

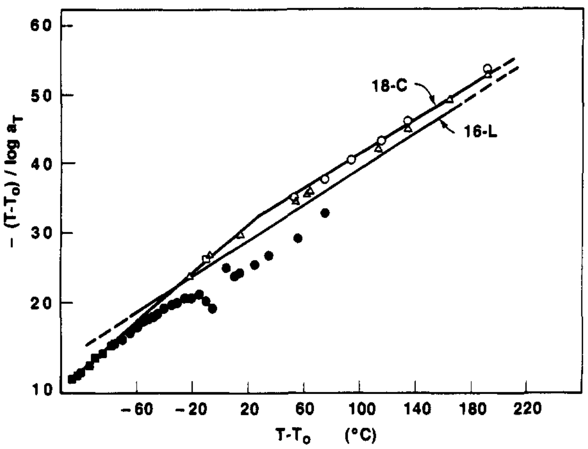

Figure 13. Comparison of time-scale shift factors for polyisobutylene from various sources. Symbols represent results from dynamic response measurements (ref 4 (●) and ref 5 (bsd)) and viscosity data (ref 4, (△) for a sample with M = 80 000 and (□) for a sample with M = 480 000).

of +50 °C or higher. Whatever the reason, however, it seems clear that the differences we find among various polyisobutylenes are not isolated incidents. It is also clear that polyisobutylenes from laboratory reactors behave conventionally, obeying a single WLF equation over the entire range of temperatures.

Finally, we note a set of still earlier measurements on a polyisobutylene sample of low molecular weight ($M \sim 4900$) by Ferry and Parks.[9] Their data on viscosity from −50 to +170 °C, recast as a_T, provide an excellent example of normal WLF behavior (Figure 14). Despite its low molecular weight, the WLF coefficients for this sample, $C_1 = 7.60$ and $C_2 = 184$ K, agree rather well with the results found here for the samples that display conventional WLF behavior.

3. Melt Viscosity–Molecular Weight Relationship. Table I lists values of $[\eta]$, the intrinsic viscosity in cyclohexane at 25 °C, for the samples used in this study. Melt viscosity η_0 at 25 °C and at 175 °C is plotted as a function of $[\eta]$ in Figures 15 and 16, respectively. When necessary, η_0 was extrapolated or interpolated from values at other temperatures using eq 4. The results at both temperatures are described fairly well by power laws

$$\eta_0 = 4.27 \times 10^7 [\eta]^{4.66} \text{ (P; 25 °C)} \qquad (13)$$

$$\eta_0 = 2.14 \times 10^4 [\eta]^{4.74} \text{ (P; 175 °C)} \qquad (14)$$

with respective correlation coefficients of 0.9981 and 0.9958. The slight displacement of C samples relative to the L and PS samples between 25 and 175 °C reflects the difference in a_T behavior for commercial reactor and laboratory reactor products, as discussed in the preceding section.

Equation 12 was used with the $[\eta]$–M relationship for polyisobutylene in cyclohexane in ref 1 to obtain the following relationship between melt viscosity and molecular weight at 25 °C.

$$\eta_0 = 4.69 \times 10^{-11} M^{3.43} \text{ (P)} \qquad (15)$$

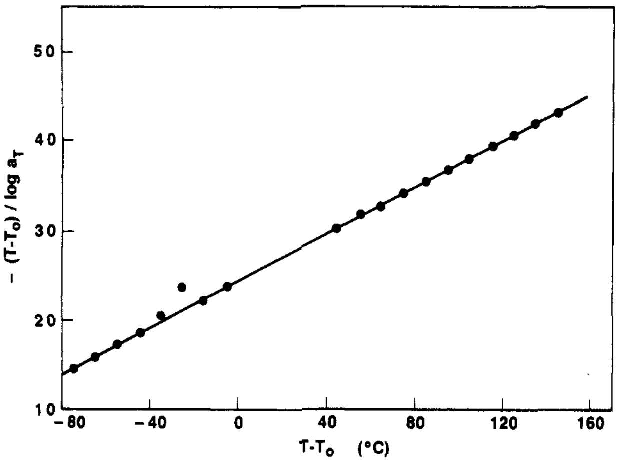

Figure 14. WLF plot of viscosity measurements for a low molecular weight polyisobutylene. Data taken from ref 9.

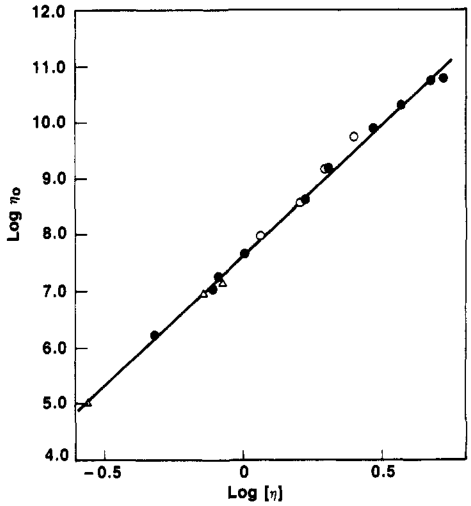

Figure 15. Melt viscosity of polyisobutylene at 25 °C as a function of the intrinsic viscosity in cyclohexane. Symbols represent data for the C series (●), the L series (○), and the PS series (△).

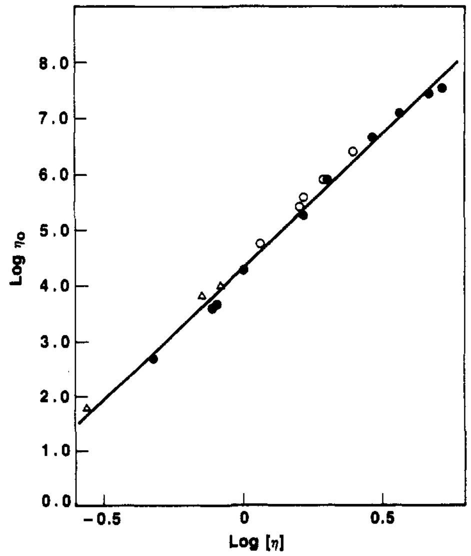

Figure 16. Melt viscosity of polyisobutylene at 175 °C as a function of intrinsic viscosity in cyclohexane. Symbols are the same as those in Figure 15.

Fox and Flory have reported melt viscosity for polyisobutylene fractions at 217 °C.[3] Their results, with revised molecular weights based on values of $[\eta]$ in cyclohexane for the same samples[10] and the $[\eta]$–M relationship in ref 1, are shown in Figure 17. The solid line is the least-squares result for our samples using melt viscosities extrapolated to 217 °C. The agreement is quite satisfactory.

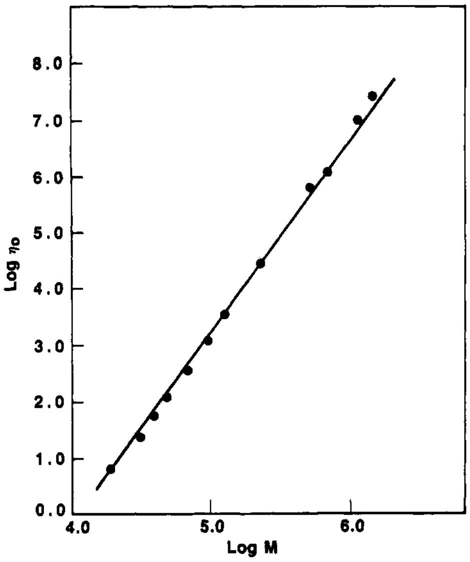

Figure 17. Melt viscosity of polyisobutylene at 217 °C as a function of weight-average molecular weight. The data are results reported in ref 3 using molecular weights that were corrected as explained in the test; the line was calculated from the data in this study as described in the text.

Summary and Conclusions

Viscoelastic properties of undiluted polyisobutylene were measured in the plateau and terminal regions for wide ranges of temperature and molecular weight and compared with the results of several earlier studies. For the most part the earlier results were confirmed, and the behavior was found to be similar to data for the melts of many other species of flexible-chain polymers. Only one exception to this general pattern of consistency was found. The products of commercial reactors, whether fractionated or not, departed somewhat from conventional WLF behavior in their dependence on temperature. Samples prepared in laboratory reactors, though not detectably different in chemical microstructure, were found to behave in a conventional manner. Earlier work on polyisobutylene, in all cases based on commercial materials, appears to show similar departures from conventional WLF behavior.

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