

1995 Bingham Medal Address: Oh, thermorheological simplicity, wherefore art thou?

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Synopsis

Polyisobutylene (PIB) was the first polymer whose viscoelastic behavior was thoroughly studied. The measurements made worldwide on the PIB sample distributed from the National Bureau of Standards were compiled and analyzed by Bob Marvin. The superposition of the data substantiated the time-temperature reduction process, which was suggested by Herbert Leaderman, first put into practice by Arthur Tobolsky, and given a theoretical foundation by John Ferry. Polymers that behaved in a like manner were called thermorheologically simple by A. J. Staverman and F. Schwarzl. Subsequently the behavior of PIB has been found to be the exception rather than the rule. The various deviations for this simplicity are briefly reviewed and PIB is reexamined. © 1996 Society of Rheology.

I. INTRODUCTION

I would like to take you on a different kind of a trip back to the future. As a student 40 years ago I thought that research was a misnomer ... that we searched anew in our investigations; but now I wish to affirm its veracity. Although Kohlrausch (1876) made his observation on “die Elastische Nachwirkung” 150 years ago, the study of the viscoelastic behavior of polymers did not start in earnest until the 1930’s and did not come into focus until the late 1940’s. However, a somewhat recent advertisement for tennis racquets stated that “Prince has brought Stealth aerospace technology to racquet design with an advanced material called viscoelastic polymer—to give unparalleled control.” Some things take a while to be appreciated and this arena of investigation is far from over.

My story today starts with polyisobutylene and ends with polyisobutylene (PIB). During the late forties and early fifties polyisobutylene was most frequently the polymer chosen for rheological studies. Many studies involved tests of the time-temperature equivalence principle. The question being addressed was ... Do the isothermally determined viscoelastic functions, such as the stress relaxation modulus, the creep compliance, and the complex dynamic modulus, remain substantially unchanged in shape as functions of the logarithmic time or frequency scales; so that, except for minor magnitude changes, the curves simply shift along the logarithmic time scale toward shorter times or toward higher frequencies with increasing temperature? If this were the case, viscoelastic functions measured over the typically available time/frequency range of $1\frac{1}{2}$ – $2\frac{1}{2}$ decades could be used to construct an extended time/frequency curve, ranging over a dozen or more orders of magnitude, from a handful of curves measured at different temperatures. With such reduced curves relaxation or retardation spectra could be determined, so that

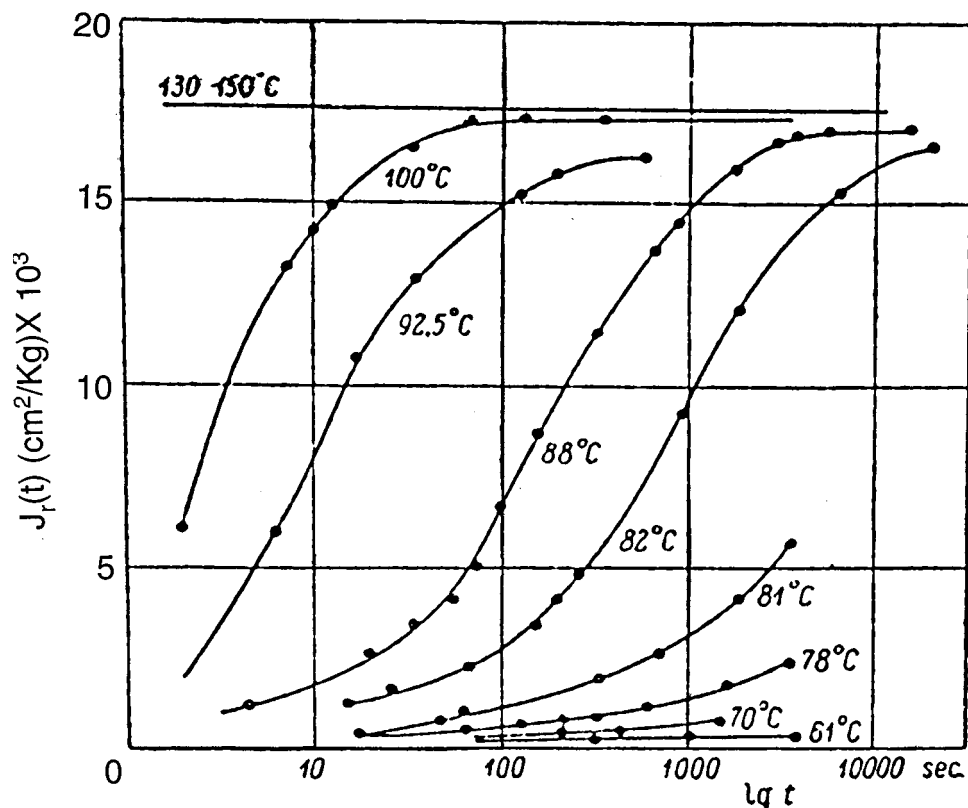


FIG. 1. The recoverable creep compliance, $J_r(t)$, of a hard rubber measured by Kobeko, Kuvshinskij, and Gurevitch (1937) highlighted by Leaderman.

structure–property relationships could be established. With only portions of a dispersion, such as that extending from the glassy to the rubbery level, the task would be much more difficult and problematic. In his book “Elastic and Creep Properties of Filamentous Materials and other High Polymers,” Herbert Leaderman (1943) presented shear recoverable creep compliance $J_r(t)$ data of Kobeko, Kuvshinskij, and Gurevitch (1937) obtained on two different rubbers [Leaderman (1943), Figs. 14 and 15] and commented: “It appears reasonable to assume that the curves in Fig. 14 for different temperatures are of the same shape, but that increase in temperature displaces the creep curve for constant load to the left: we can then say that increase of temperature has the effect of contracting the time-scale of primary creep.” [Leaderman (1943), p. 30]. The data commented on are shown in Fig. 1. He made a similar comment on the data shown in his Fig. 15, and schematically illustrated how results obtained within the “range of observation” are related to the complete dispersion, which is believed to be present at all temperatures, on p. 35 [Leaderman (1943)].

Whereas Leaderman was considered to be the King of Creep during the 40’s and 50’s, Arthur V. Tobolsky was the King of Stress Relaxation from the 40’s through the 60’s and John D. Ferry was the King of Dynamic Mechanical Properties from the 50’s through the 70’s.

It was Tobolsky with Rodney D. Andrews that produced and presented the first reduced curve (which they called a “master curve”) of actual data to the literature in 1945

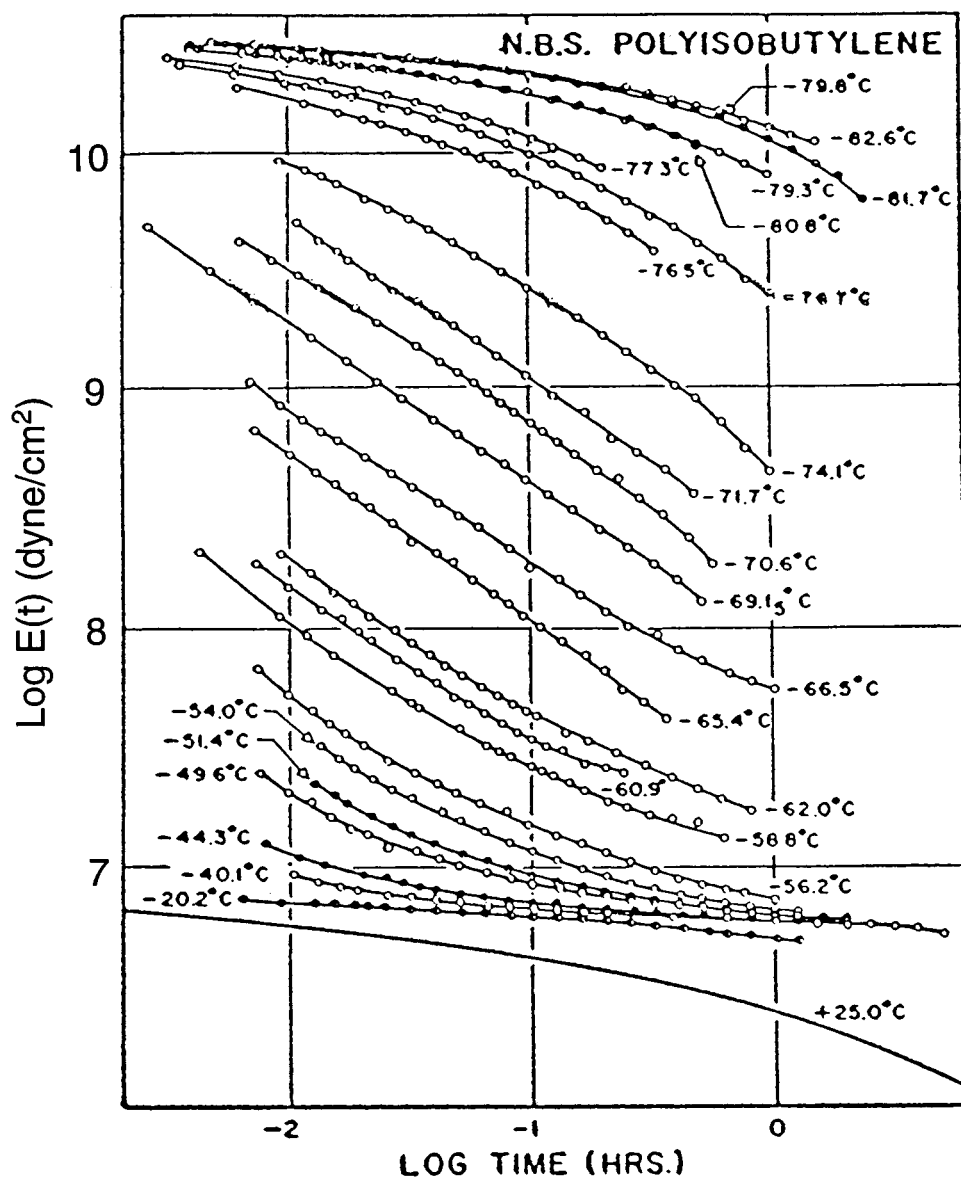


FIG. 2. Logarithmic plot of the elongational stress relaxation modulus $E(t)$ as a function of $\log t$. Data of Catsiff and Tobolsky on the NBS PIB. By permission [Catsiff and Tobolsky (1955)].

[Tobolsky and Andrews (1945)]. Five years later Ferry presented the theoretical structure for the temperature reduction process in terms of a distribution of discrete relaxation mechanisms [Ferry (1950)].

During the early 50's a plethora of data mostly obtained on polyisobutylene provided what appeared to be a firm foundation for successful time-temperature reduction. Certainly, not all, but a great deal of the data was obtained on the National Bureau of Standards PIB which was distributed throughout the world by Robert S. Marvin to provide a database so that the newly developed techniques for studying the markedly time-

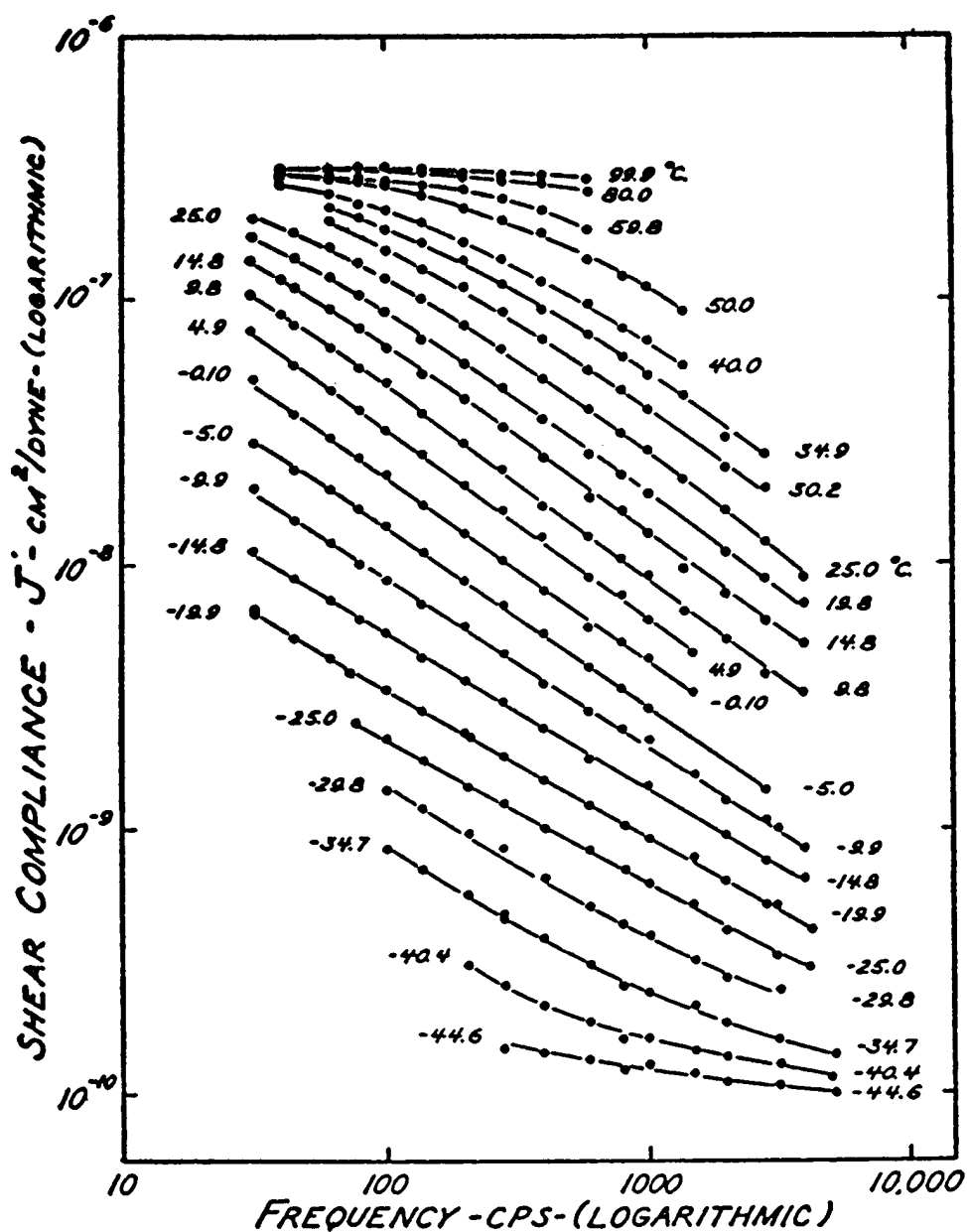


FIG. 3. Variation of the real part of the dynamic shear compliance J' with frequency for the National Bureau of Standards Polyisobutylene ($M = 1.35 \times 10^6$) at 22 temperatures as indicated. By permission [Fitzgerald, Grandine, and Ferry (1953)].

dependent properties of polymers could be assessed. Results of the "cooperative program to determine the viscoelastic properties of high molecular weight polyisobutylene" where the general features of the distribution functions of the relaxation and retardation times of a high molecular weight amorphous polymer which ranged from the glassy level of response, out to the long-time steady-state response [Marvin (1953)]. The various inves-

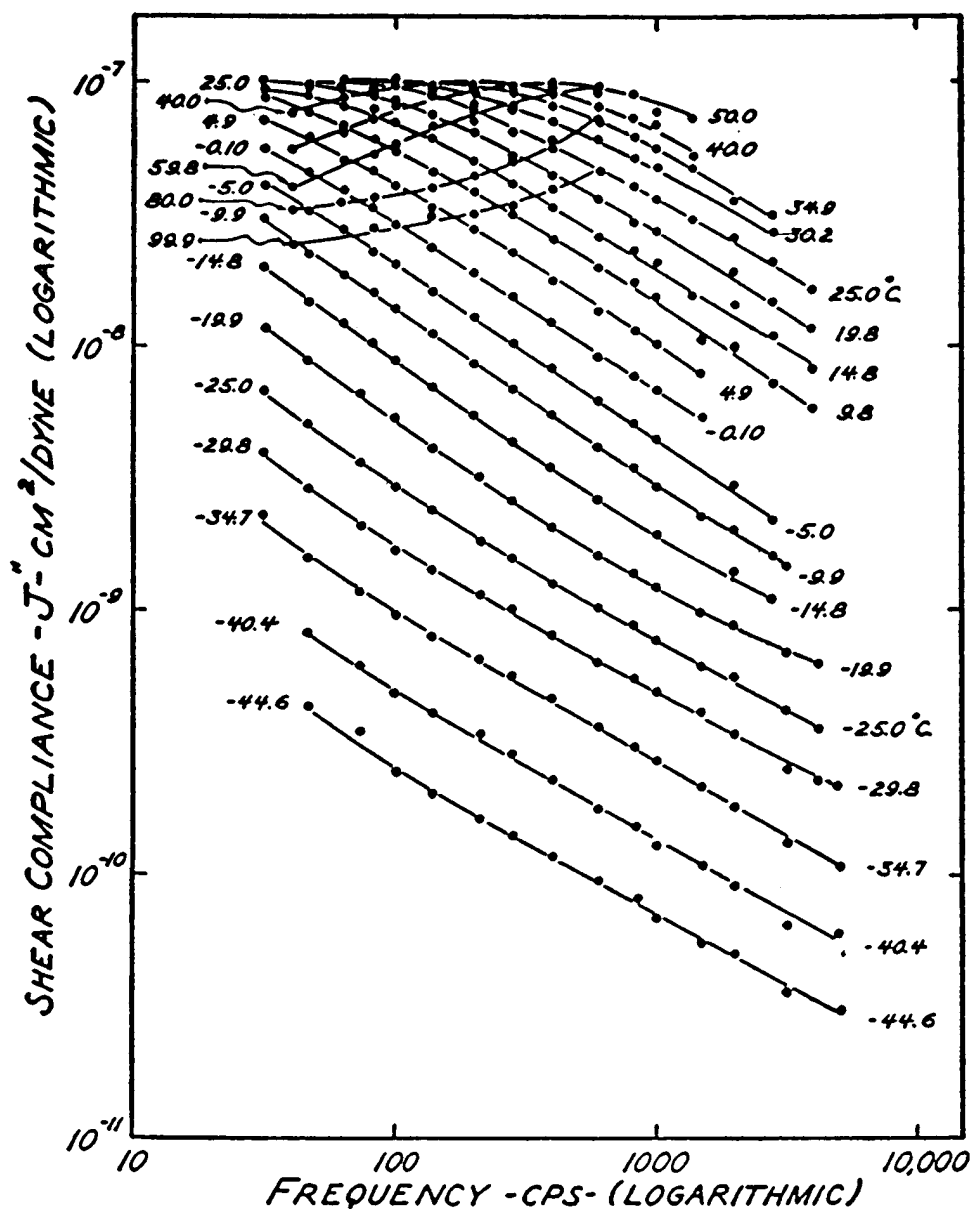


FIG. 4. Variation of the imaginary part of the dynamic shear compliance J'' with frequency for the NBS PIB. By permission [Fitzgerald, Grandine, and Ferry(1953)].

tigators covered a combined time/frequency range of 15 decades. The long list of participants is given in Marvin (1953). The most extensive sets of data were stress relaxation results contributed by Andrews and Tobolsky and dynamic results of Ferry, Fitzgerald, and Grandine; and those of Fletcher and Gent.

The elongational stress relaxation moduli $E(t)$ of the NBS PIB, presented by Catsiff and Tobolsky (1955), are shown in Fig. 2. The dynamic results obtained by forced shear oscillation measurements on the NBS PIB by Fitzgerald, Grandine, and Ferry (1953) are

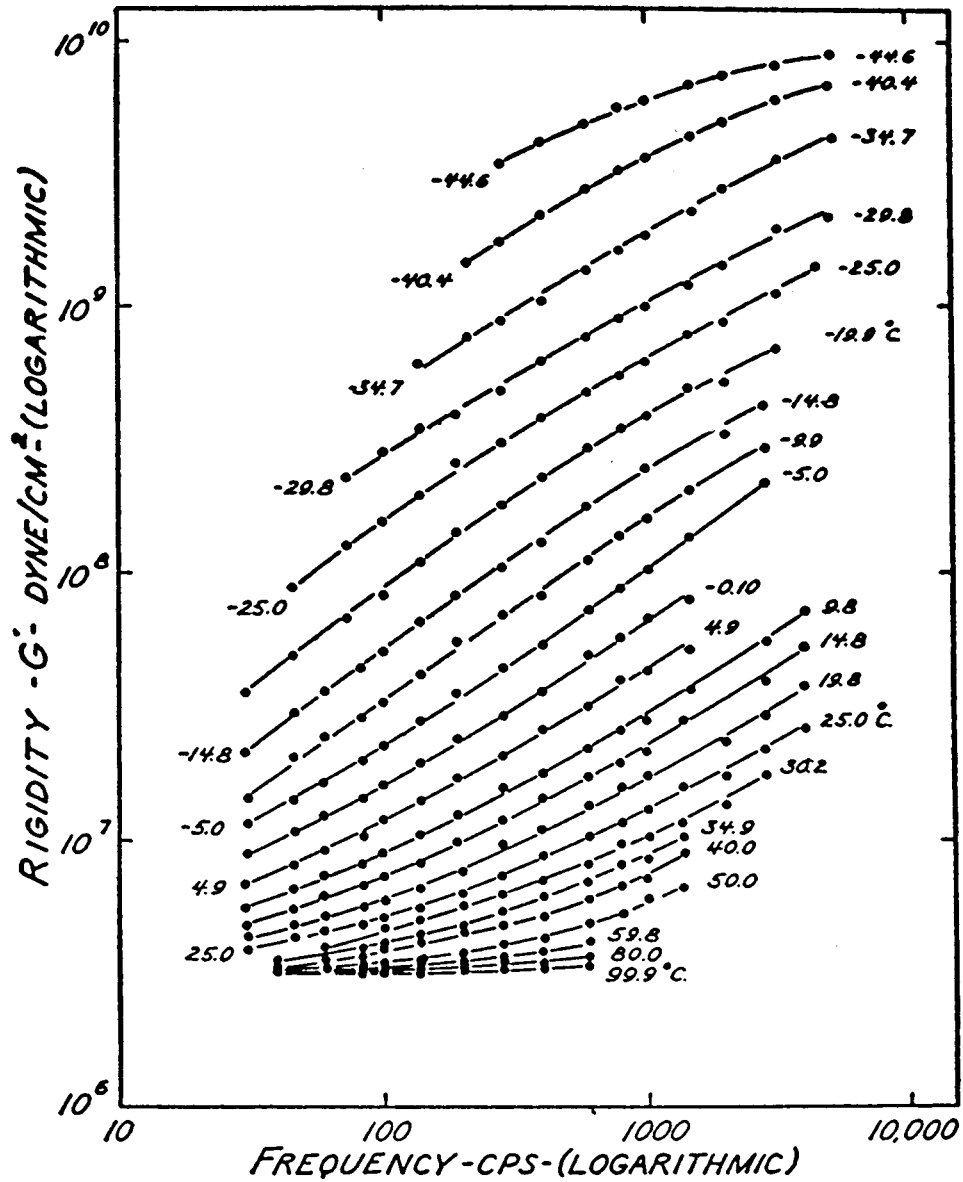


FIG. 5. Variation of the real part of the dynamic rigidity G' with frequency for the NBS PIB. By permission [Fitzgerald, Grandine, and Ferry (1953)].

shown in terms of the real J' and imaginary J'' components of the complex dynamic shear compliance, $J^*(\omega) = J' - iJ''$ and the real G' component of the complex dynamic shear modulus, $G^*(\omega) = G' + iG''$, and the real η' component of the complex dynamic shear viscosity, $\eta^*(\omega) = \eta' - i\eta''$, all as functions of the logarithmic frequency ν (Hz) in Figs. 3, 4, 5, and 6. The logarithm of the reduced storage J'_p and loss J''_p components of J_p^* are shown as functions of the logarithmic reduced circular frequency ωa_T in Figs. 7 and 8; where $J'_p = J_g + (J' - J_g)(T\rho/T_0\rho_0)$; J''_p

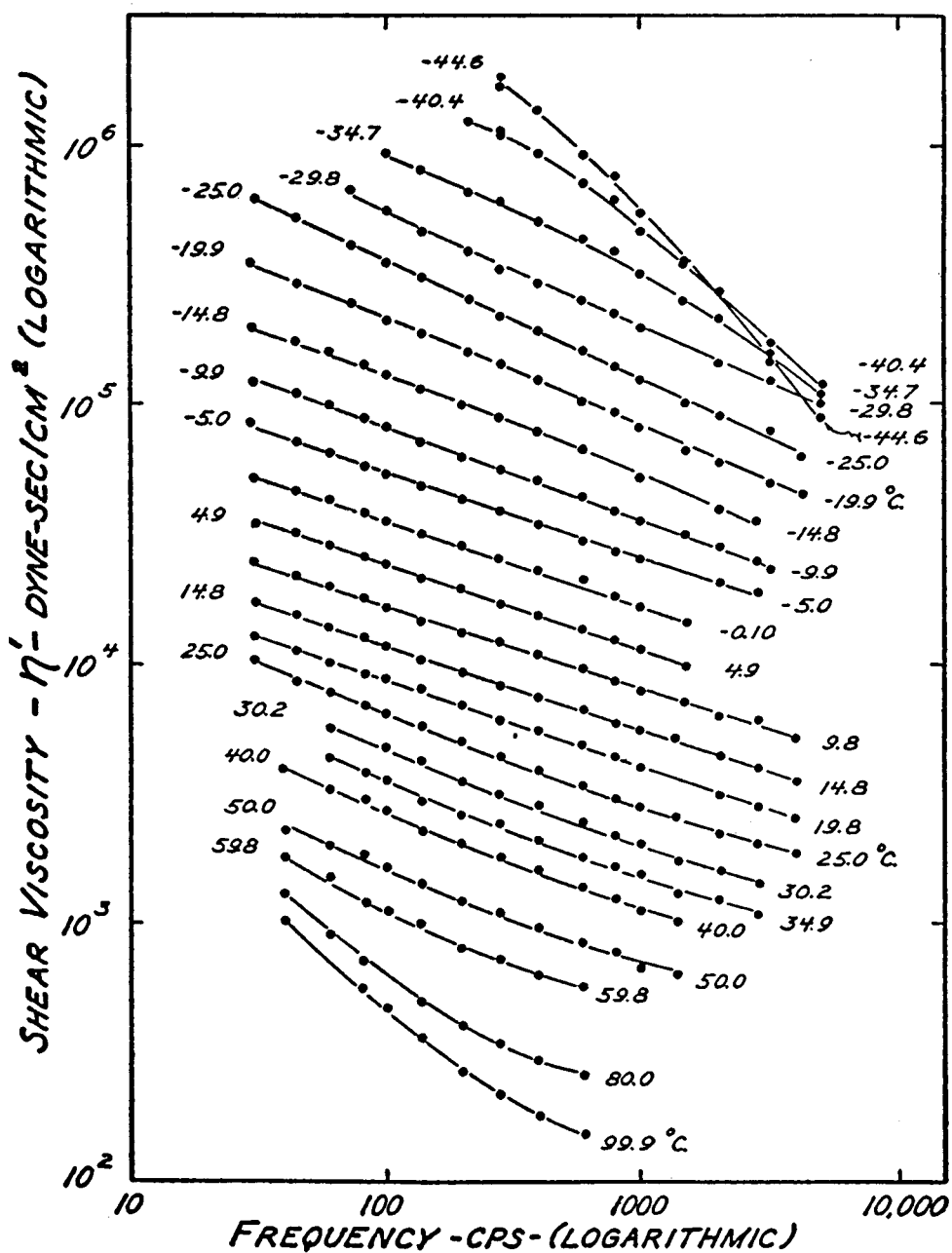


FIG. 6. Variation of the real part of the dynamic shear viscosity η' with frequency for the NBS PIB. By permission [Fitzgerald, Grandine, and Ferry (1953)].

= $J''(T\rho/T_0\rho_0)$; J_g is the glassy compliance; $\omega = 2\pi\nu$; a_T is the shift factor; ρ is the density of the sample at the temperature, T , of measurement, and ρ_0 is the density at the chosen reference temperature T_0 . These reduced curves show such excellent superposition of the curves obtained over a 144 °C temperature range that they along with the

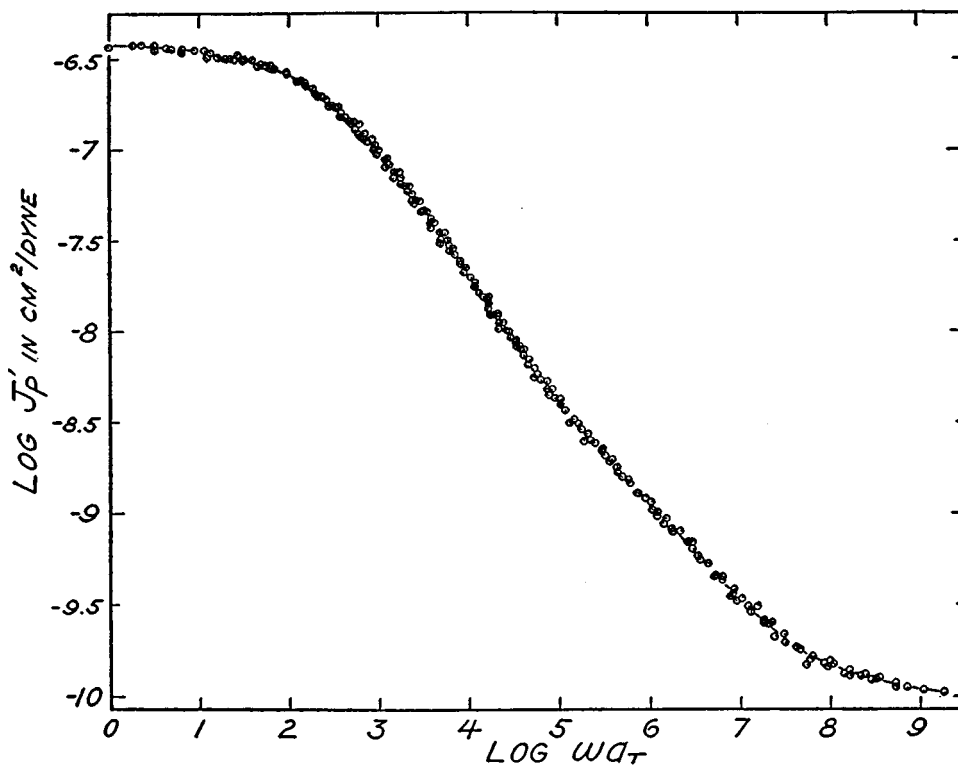


FIG. 7. Real part of the complex compliance of NBS PIB reduced to 25 °C, plotted logarithmically against the reduced frequency. By permission [Ferry, Grandine, and Fitzgerald (1953)].

reduced stress relaxation curve of Catsiff and Tobolsky (1955); and the reduced creep recovery curves of Leaderman, Smith, and Williams (1954, 1959) for a series of PIBs ranging in average molecular weight from 1.60×10^3 to 1.3×10^5 provided a firm foundation for what Schwarzl and Staverman (1952) called thermorheological simplicity.

Successful superposition of viscoelastic curves measured at different temperatures “proved” that all of the molecular mechanisms involved had the same temperature dependence. The evidence that showed this was true for polymer chain backbone motions was compelling in the 50’s; so much so, that I, as a student, knew that the viscosities that I measured on a solution of cellulose nitrate were wrong, since their temperature dependence did not agree with that of the shift factors for the dynamic behavior. Without telling Professor Ferry that I had made some bad measurements I put the results in a drawer and forgot about them.

SIDE GROUP MOTIONS

However, it was recognized that the motions of different kinds of molecular moieties, such as side groups, exhibited different temperature dependencies and hence measurements that included contributions from side groups should not be reducible. Child and Ferry (1957) found this to be the case for poly (*n*-butyl methacrylate) where the ester side group motions contribute additively to the compliance in the same region of the frequency scale as the local chain backbone motions. The consequent reduction failure

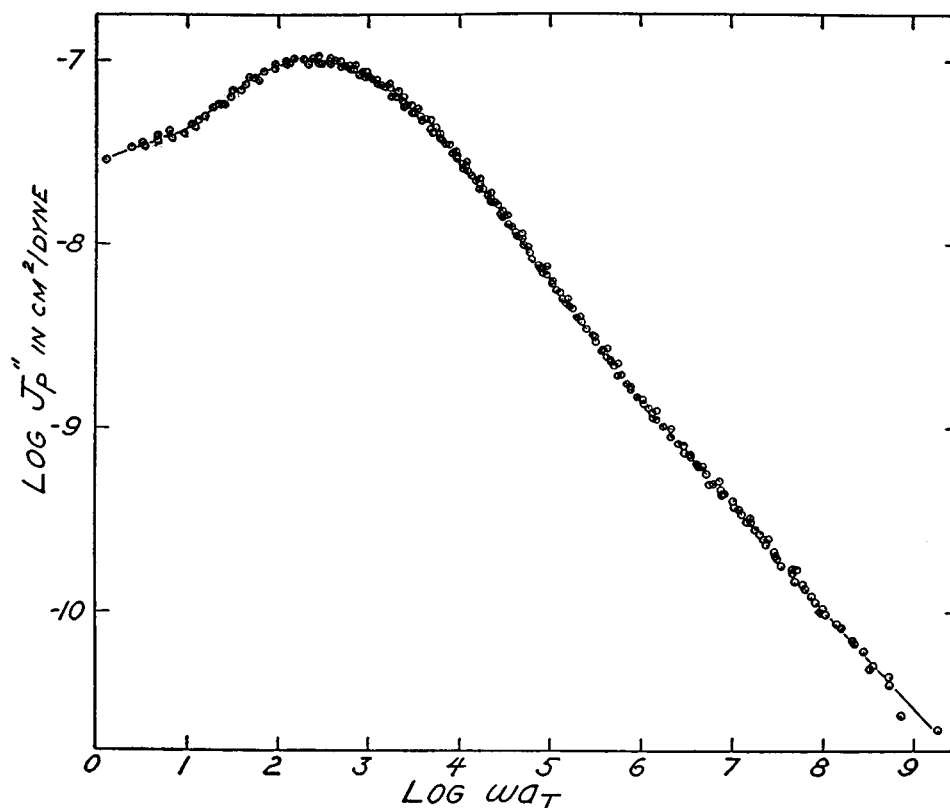


FIG. 8. Imaginary part of the complex compliance of NBS PIB reduced to 25 °C, plotted logarithmically against the reduced frequency. By permission [Ferry, Grandine, and Fitzgerald (1953)].

can be seen in Fig. 9. When observed separately from chain backbone motions (the α mechanism) the secondary dispersions or relaxations (β , γ , and δ , when observed) show successively, weaker temperature dependences with decreasing temperature and/or shorter times (higher frequencies) [McCrum, Read, and Williams (1967); Ferry (1980)]; i.e., apparent activation energies have been found to be lower for mechanisms which are seen at lower temperatures or shorter times.

TROUBLE IN THE RUBBERY PLATEAU

In 1959 a different kind of reduction failure was observed by Berge, Saunders, and Ferry (1959) in the entanglement plateau zone [Ferry (1980)], as can be seen in Fig. 10 where the logarithm of J_p'' is shown as a function of $\log \omega a_T$. It was hypothesized at the time that the lack of reduction was due to a changing entanglement concentration with a change in temperature. Ferry and I are of the opinion that this hypothesis deserves further testing and investigation.

DIFFERENT TEMPERATURE DEPENDENCES FOR SOFTENING AND VISCOUS FLOW

Some eight years after secreting my "bad" viscosity data, I completed my first study on a "monodisperse" polystyrene ($M = 47\,000$) [Plazek (1965)] with my frictionless

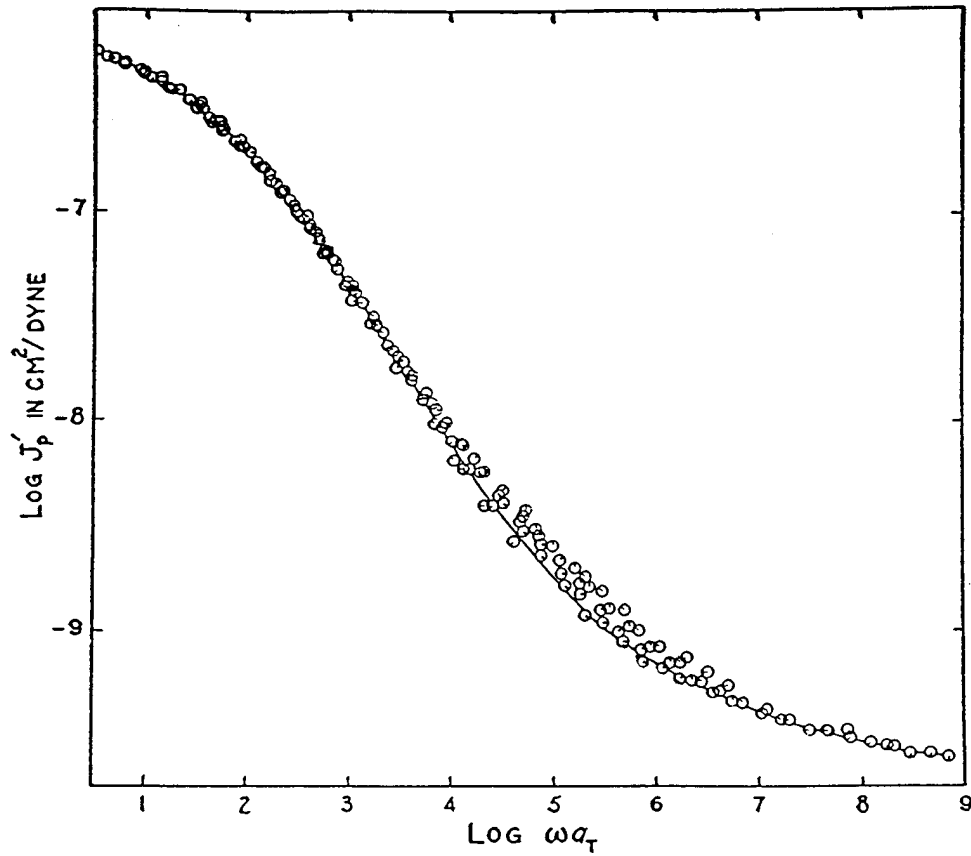


FIG. 9. Real part of the complex compliance J' , for a fraction of a poly (*n*-butyl methacrylate) reduced to 100 °C and plotted logarithmically against the reduced frequency. The solid curve represents the probable compliance of the α mechanism. By permission [Child, Jr. and Ferry (1957)].

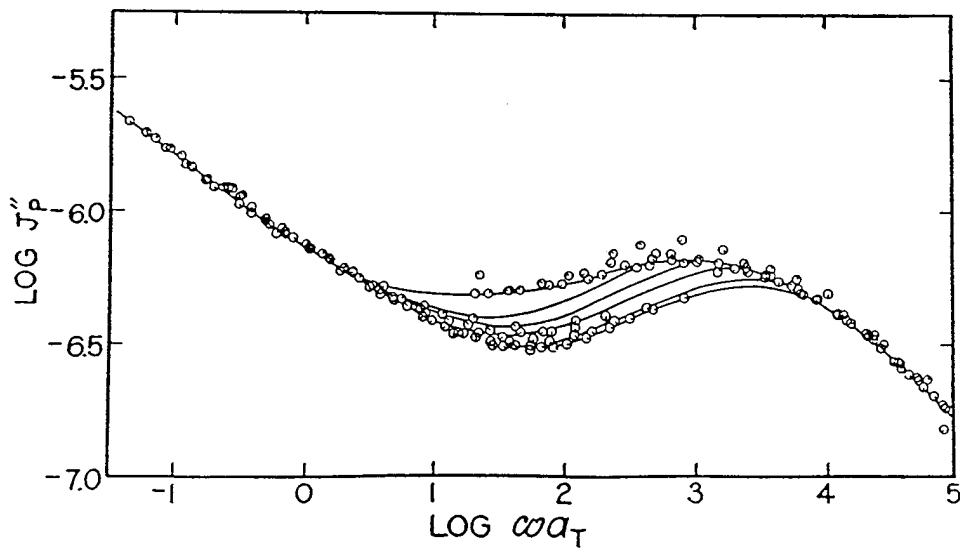


FIG. 10. Imaginary part of the complex compliance J'' for a poly (*n*-octyl methacrylate) as a function of the logarithm of the reduced frequency ωa_T , where $\omega = 2\pi\nu$. ν is the frequency in Hz (cps). $T_0 = 100$ °C. By permission [Berge, Saunders, and Ferry (1959)].

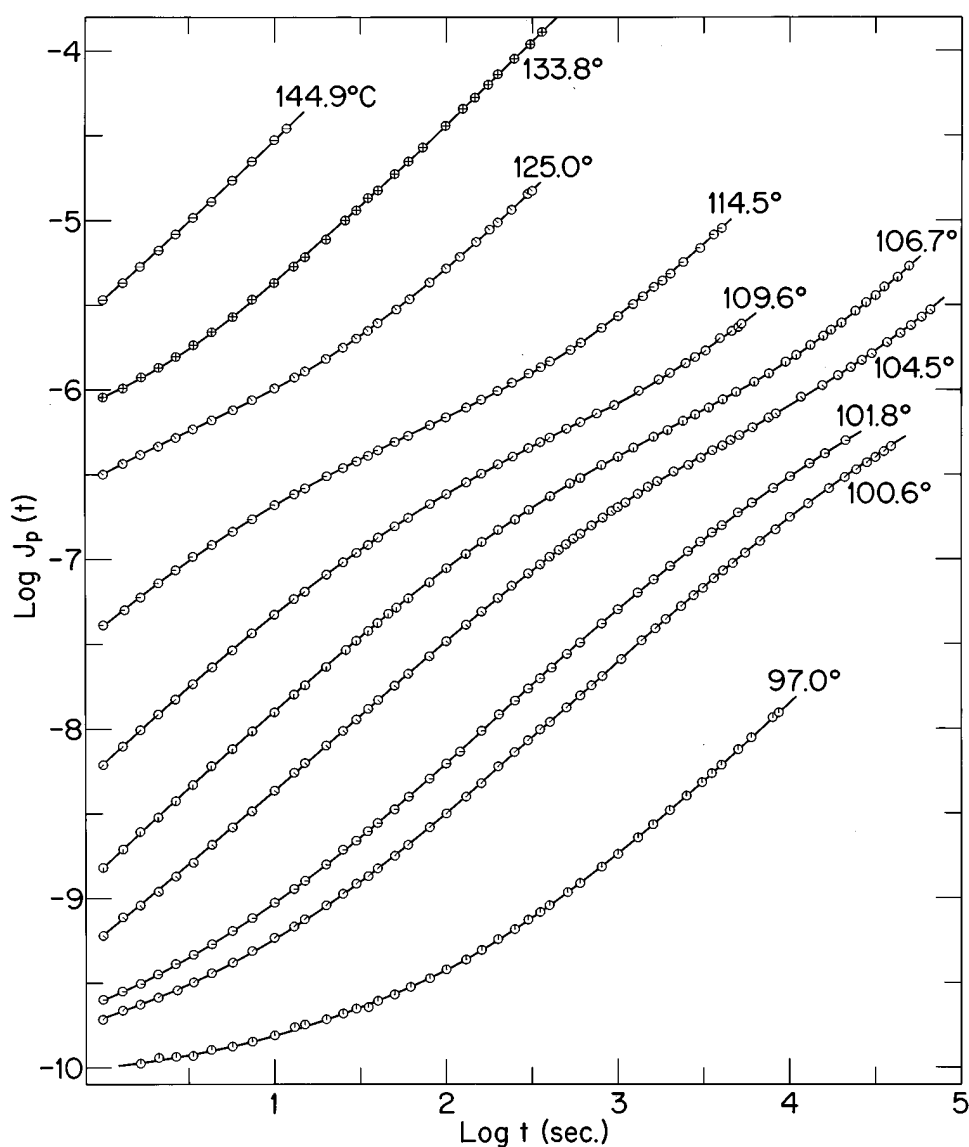


FIG. 11. The creep compliance $J_p(t)$, cm^2/dyn , of polystyrene, $M_w = 46\,900$, plotted logarithmically against the time, s. Temperatures of measurement are indicated. The subscript p indicates amplitude adjustment for the temperature dependence of the rubberlike nature of the response [Plazek (1965)].

creep apparatus [Plazek (1968)]. I was surprised that, while the recoverable compliance curves $J_{r,p}(t)$ reduced satisfactorily, the creep compliance curves did not. Figures 11 and 12 show the as-measured and reduced $J_p(t)$ curves. The viscosity shift factors $a_{T,\eta} = \eta(T)T_0\rho_0/\eta(T_0)T\rho$ were used to reduce the $J_p(t)$ curves. The long-time results reduce well because the viscous deformation dominates the terminal zone; whereas the curves in the glass-to-rubber dispersion are spread over a logarithmic decade of the reduced time. The reduced recoverable compliance curves

$$J_{r,p}(t) = (J(t) - t/\eta)_p$$

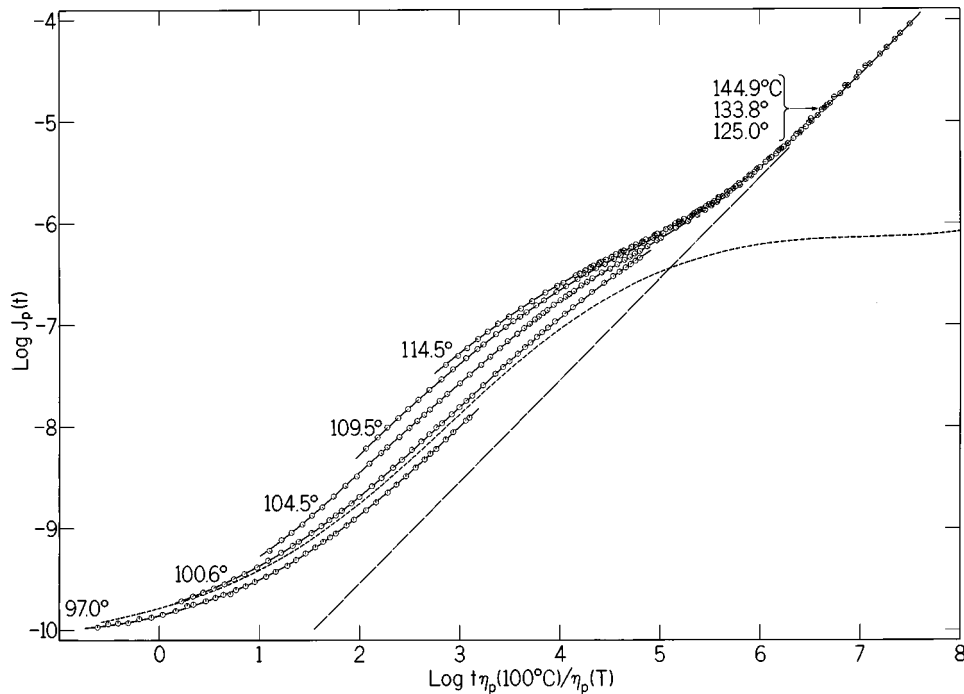


FIG. 12. Logarithmic plot of creep compliance, $J_p(t)$ against reduced time scale t/a_T , $a_T = \eta_p(T)/\eta_p(T_0)$, $T_0 = 100^\circ\text{C}$. Failure of temperature reduction is indicated. The long-dashed line is the 100°C t/η contribution. The short-dashed line is the reduced recoverable compliance curve (polystyrene $M_w = 46900$) [Plazek (1965)].

can be seen to be successfully reduced in Fig. 13 with a temperature dependence that was different from that of the viscosity. The final slight dispersion, seen at reduced times greater than 10^8 s is due to an otherwise undetectable high molecular weight tail. Hence the plateau seen represents J_s the steady state recoverable compliance and not a rubbery entanglement plateau as originally surmised [Plazek (1965)].

FALLACIOUS REDUCTIONS

With data taken within a fairly narrow experimental window (3 decades of time or frequency or less) the test for thermorheological simplicity can only be definitive in its failure: i.e., thermorheological complexity can be proven, simplicity cannot. To illustrate this we have taken the $J_p(t)$ data points obtained on a narrow distribution polystyrene PS-L5 ($M = 1.22 \times 10^5$) at times equal to or less than 1000 s and reduced them to a common curve [Plazek (1968)]. The full data set, covering up to 6 decades of time, is shown in Fig. 14. The curtailed reduced data set, covering 3.4 decades of time, is shown in Fig. 15 where only a slight deviation from complete superposition is seen at the beginning of the rubber plateau. However, the data at long reduced times, which were obtained at the highest temperatures of measurement, show excellent superposition; but the position of the viscous deformation line t/η predicts a viscosity at the chosen temperature of reduction, $T_0 = 100^\circ\text{C}$ that is about ten times too high. The correct t/η line is indicated by the solid straight line. It was obtained by using the viscosities obtained at temperatures between 114 and 200°C . The paper which presented this example of falla-

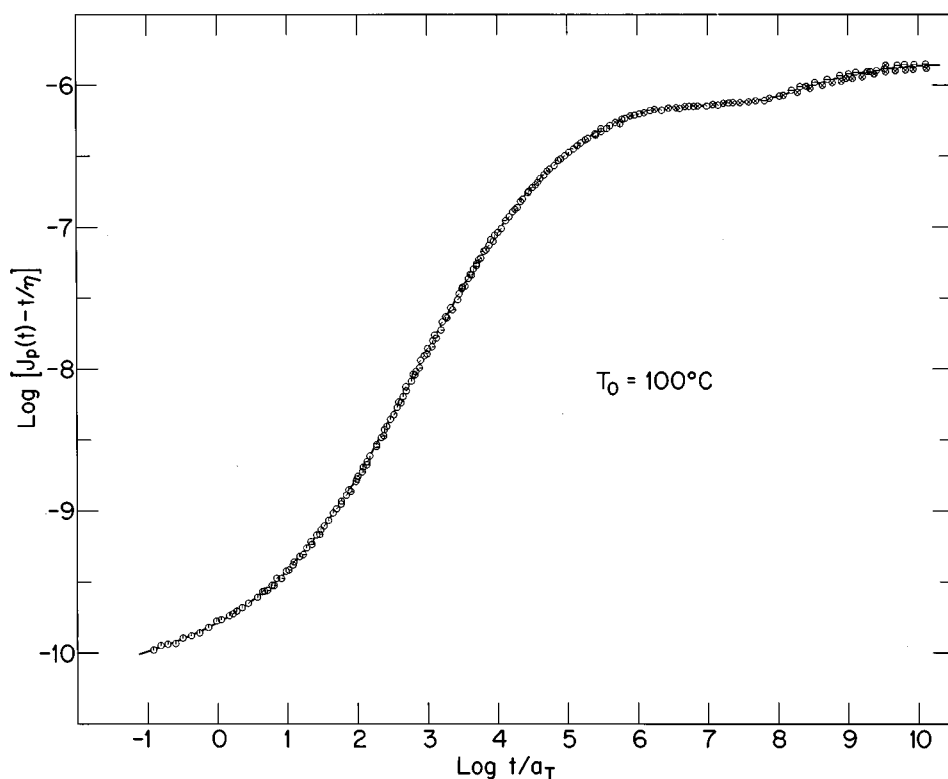


FIG. 13. Logarithmic plot of recoverable compliance, $J_p(t) - t/\eta$, against reduced time, t/a_T , reduced to 100°C for polystyrene ($M_w = 46\,900$) [Plazek (1965)].

cious reduction was reviewed, at the time, by a past president of the Society of Rheology, Jim Bergen, who in his comments said that I had presented my argument with “devastating clarity.” This was a compliment which I have cherished over the years.

Using all of the recoverable compliance data obtained on PS-L5, the failure of reduction as the rubbery plateau is approached is seen to be serious, in itself. This is clearly seen in Fig. 16. I reported this failure in 1968 and it was rediscovered nearly 20 years later; see below.

TWO TEMPERATURE DEPENDENCIES OF THE RECOVERABLE COMPLIANCE

It was not until I measured a polyvinylacetate [Plazek (1980)] sample, which exhibited a steady-state recoverable compliance, J_s , which was substantially greater than the entanglement plateau compliance, J_N , that the temperature dependence of the recoverable compliance, $J_r(t)$ in the terminal dispersion was found to be different from that in the glass to rubber softening dispersion: the latter being stronger. The temperature dependence of $J_r(t)$ in the terminal dispersion was found to be the same as that of the viscosity. The as measured curves are seen in Fig. 17. Because of the difference in temperature dependences the rubbery plateau length changes with temperature.

As the temperature is decreased toward the glass temperature T_g the softening dispersion moves toward longer times faster than the terminal dispersion and the plateau short-

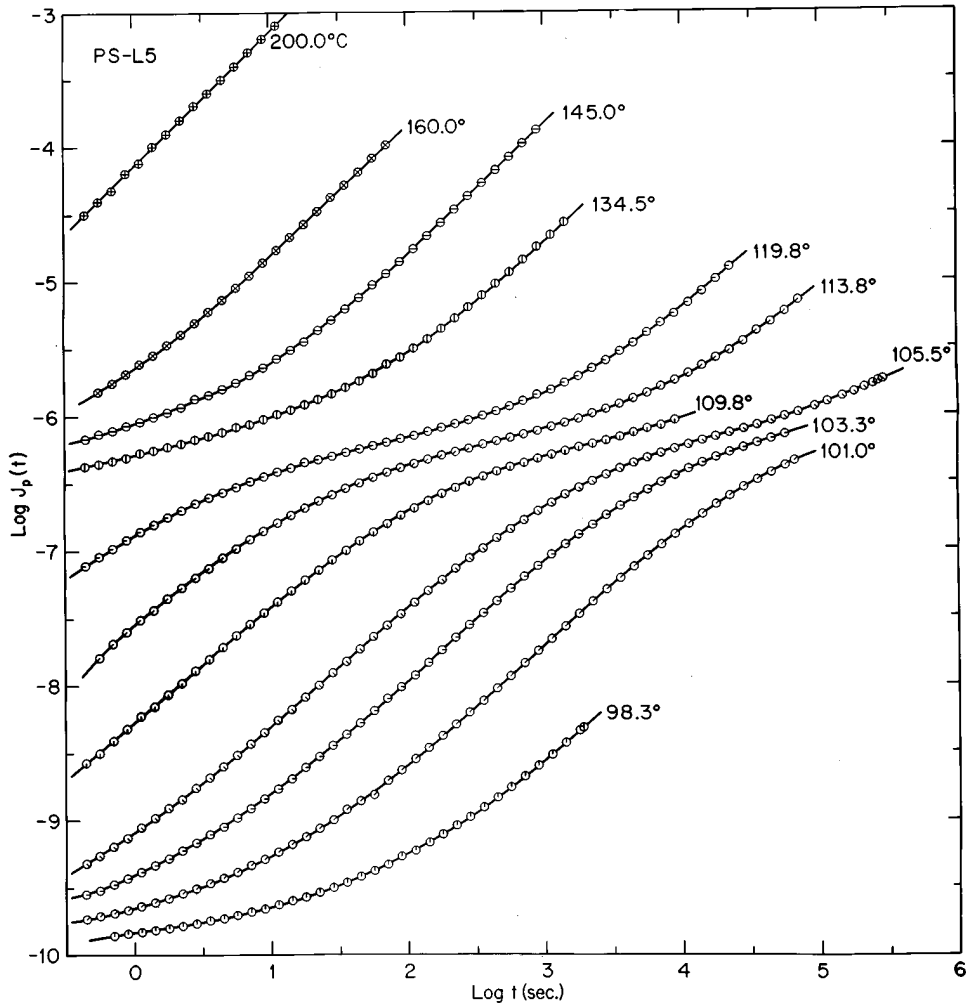


FIG. 14. Logarithm of creep compliance curves $J_p(t)$ (in square centimeters per dyne) plotted as a function of logarithm of the time for polystyrene sample L-5, molecular weight 1.22×10^5 . Results at eleven temperatures between 98 and 200 °C are presented. The subscript p indicates that the rubberlike temperature dependence has been taken into account. $J_p(t) = J(t)T\rho/T_0\rho_0$ [Plazek (1968)].

ens. Note that this is contrary to the general trend of temperature dependences mentioned above, i.e., mechanisms at shorter times or lower temperatures have a weaker temperature dependence. The change in plateau length is illustrated in Fig. 19 where the best possible reduction of the data from Fig. 18 is shown reduced to two different temperatures 35 and 60 °C. At 35 °C the length of the plateau can be seen to be 25 times shorter than at 60 °C.

INCREASE OF THE TAN δ PEAK WITH DECREASING TEMPERATURE

In 1987 Cavaille *et al.* (1987) found that their dynamic measurements on a polystyrene ($M_n = 98,000$; $H.I. = 1.12$) yielded results that did not reduce. Most dramatically, a linear plot of the loss tangent, $\tan \delta$, as a function of the logarithmic frequency revealed a peak value that increased by 50% as the temperature was decreased from 100.7 to 91.3 °C; see Fig. 19. Fortunately, or unfortunately, depending on one's view-

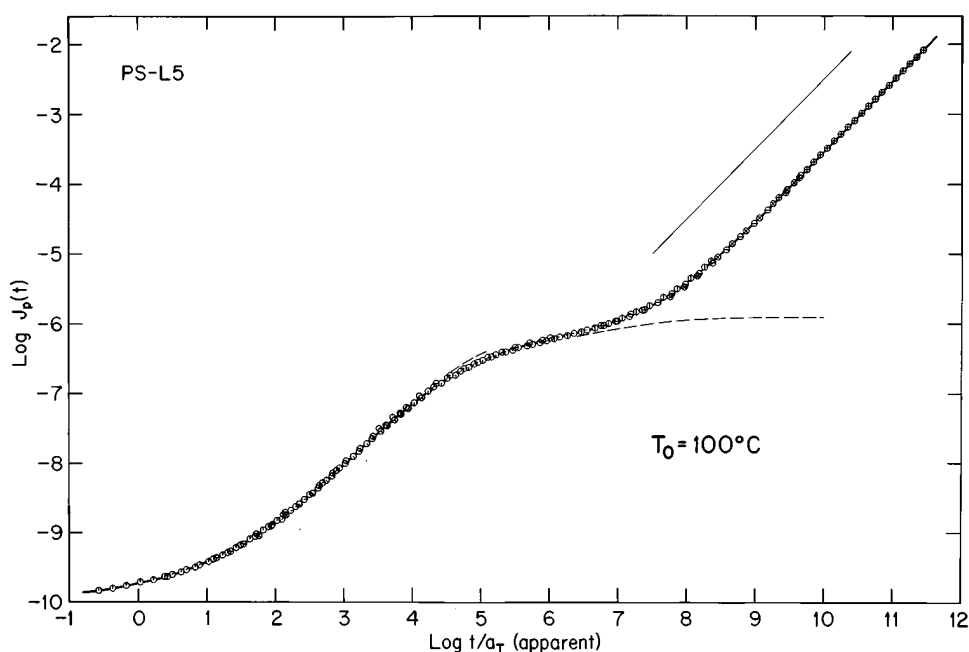


FIG. 15. Apparent temperature reduction to 100 °C of data shown in Fig. 14 at times less than 1000 s; (---)recoverable compliance; solid line with a slope = 1, the true position of the dominating viscous component, t/η , of the creep compliance at 100 °C. The apparently successful reduction has resulted in an order of magnitude error in this terminal region of response.

point, as a reviewer of their manuscript I was obliged to point out to the authors that “I did that nearly 20 years ago” (as Wladimir Philippoff was wont to say frequently at the Annual Meetings of the Society of Rheology during the 50’s and 60’s. His justified claims, entertained many of the younger members of the Society, such as myself). The increasing slope, with decreasing temperature, of the recoverable creep compliance curves as the rubbery plateau is approached in Fig. 16, is a reflection of the change of the $\tan \delta$ peak seen in Fig. 19. A more recent conformation of this example of thermorheological complexity can be seen in Fig. 20. These data were obtained on a commercial polystyrene sample (D685) by Richard Connelly of the Kodak Corp. [Personal communication]. This kind of non-reducibility is characteristic of high molecular weight amorphous polymers which have a relatively high steepness factor [Plazek and Ngai (1991)] $S = -T_g [d \log a_T / dT]_{T_g} \geq 100$, or equivalently, a high coupling constant ($n \geq 0.55$) of the Ngai coupling theory [Ngai (1990)].

LOW MOLECULAR WEIGHT ANOMALIES

J_S is insensitive to temperature changes in the range, $1.1 < T/T_g < 2.0$, where T is in Kelvins [Plazek and Chelko (1977)]. However, at least for low molecular weight polymers, where J_S can be measured in the range $1.0 < T/T_g < 1.1$ it shows a dramatic decrease as T_g is approached from above [Plazek and O’Rourke (1971)]. For a polystyrene with a narrow molecular weight distribution and $M = 3400$ J_S was found to diminish 30-fold as the temperature was decreased from 100.6 to 70.0 °C. The data in Fig. 21 were reduced by shift factors determined from measurements on a series of polystyrenes of differing molecular weights. The increases in $J_r(t)$ at reduced times greater than 1 s

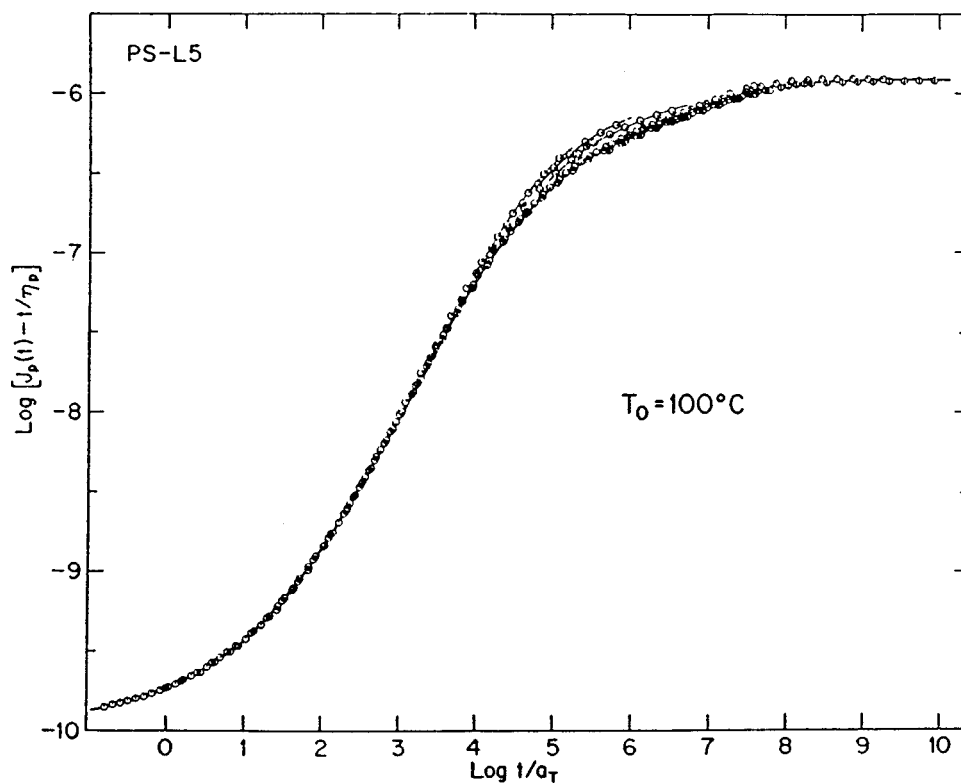


FIG. 16. Attempted reduction to 100 °C of the recoverable compliance data for PS-L5. $\text{Log } J_{r,p}(t)$ is shown as a function of reduced logarithmic time, $\text{log } t/a_T$, where a_T is the usual temperature shift factor [Plazek (1968)].

have been shown to be attributable to a small high molecular weight tail, since other samples which were fractions of anionically polymerized polystyrene do not show this pronounced terminal behavior. As an example, Fig. 22 shows the recoverable compliance behavior of another narrow distribution polystyrene {TAPS 28, $M = 12\,300$ [Ngai, Plazek, and Deo (1987)]}. J_S has been shown to be the most sensitive parameter of the molecular weight distribution [Mills and Nevin (1971); Ninomiya, Ferry, and Ōyanagi (1963)]. Small amounts of high molecular weight molecules are in a highly diluted state and are the only moities that are viscoelastically active at long times. These molecules are enormously elongated at the higher shear rates present when they are surrounded by molecules with a much lower molecular weight at a given stress level. The consequent high level of orientation of the longer molecular chains, created during creep, leads to the large recoverable strains observed.

The spectra in Fig. 23 were extracted from the recoverable compliance curves of Fig. 21 [Riande *et al.* (1975)]. The $L(\ln \tau)$ seen at 70 °C, which is the glass temperature T_g of this low molecular weight sample, is characteristic of a nonpolymeric organic glass-former [Plazek and Magill (1966); Plazek, Bero, and Chay (1994a)]. It has a single maximum preceded by a line with a slope of 1/3. The marked positive curvature leading to a relatively narrow peak at the higher temperatures is believed to represent contribu-

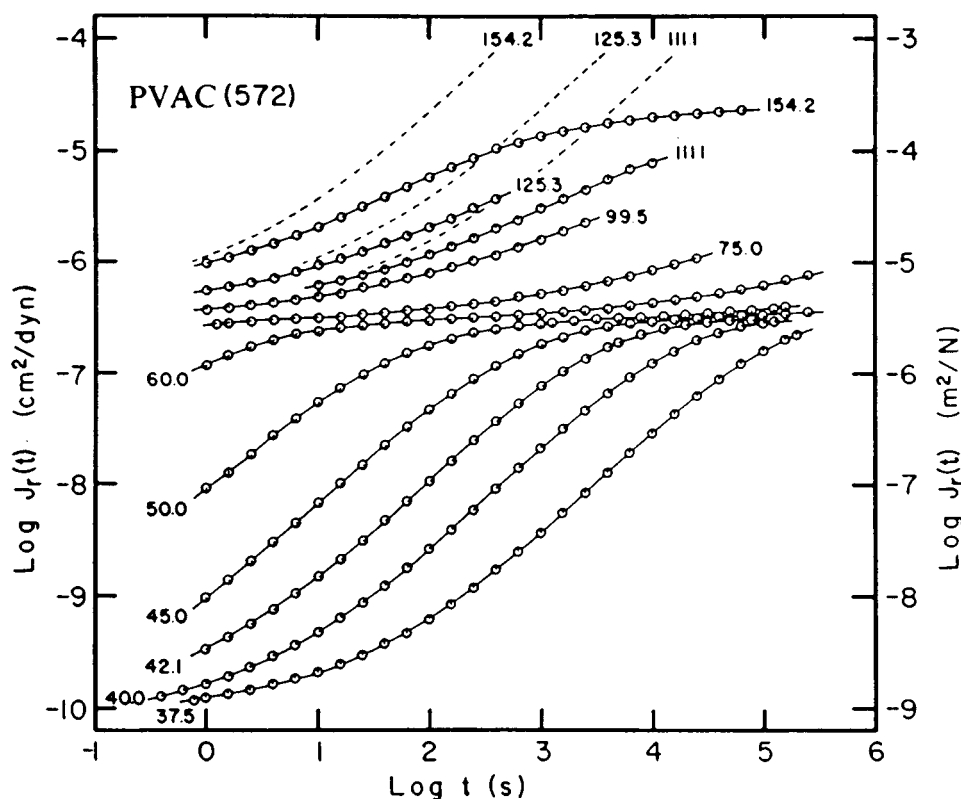


FIG. 17. Logarithmic plot of the recoverable shear compliance, $J_r(t)$, $\text{cm}^2 \text{dyn}^{-1}$, as a function of time (s), for a poly(vinyl acetate) sample ($M_w = 6.5 \times 10^5$) at 11 temperatures in $^\circ\text{C}$. Dashed lines indicate the total creep compliance, $J(t)$, determined at the three highest temperatures of measurement [Plazek (1980)].

tions to the recoverable deformation by polymeric Rouse and sub-Rouse modes of motion [Ngai and Plazek (1995)]. Polymeric modes of motion are lost with decreasing temperatures as T_g is approached.

This unusual and surprising behavior has been confirmed for polystyrene by Gray, Harrison, and Lamb (1976) using dynamic measurements; see Fig. 24. It has also been observed in poly (methylphenylsiloxane) [Plazek *et al.* (1994b)]. Complementary explanations for the loss of polymeric modes have been given by Ngai, Plazek, and Deo (1987, 1993)]. Figure 25 shows how J_s diminishes with decreasing temperature for different molecular weight polystyrenes. The evolution of the retardation spectrum of polystyrene with molecular weight is presented in Fig. 26, where the results obtained on four samples, A67 ($M = 1100$), PC-11 (3400), A61 (16 400), and A19 (600 000). The chosen reference temperature for all of the materials was 100°C . Since the molecular weight per entangled unit M_e is 17 000 only A19 possesses an entanglement network. The softening dispersions for the lower molecular weight samples appear at shorter reduced times at 100°C because their T_g 's are progressively lower, i.e., T_g (A19) $\approx 97.8^\circ$; (A61) $\approx 91.5^\circ$; (PC-11) $\approx 70^\circ$, and (A67) $\approx 40^\circ\text{C}$ [Plazek and O'Rourke (1971)].

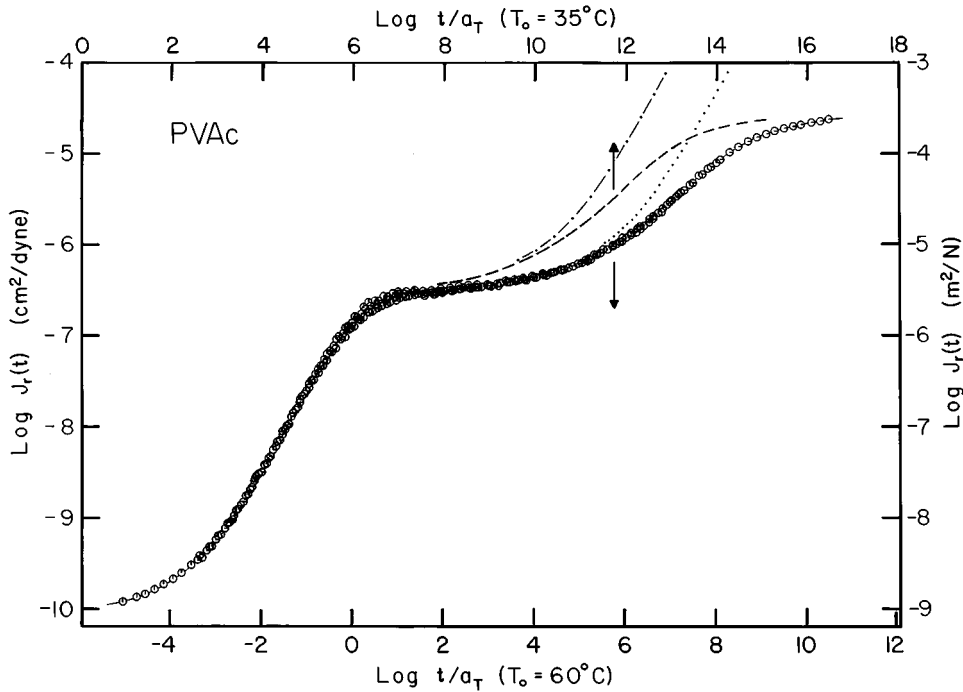


FIG. 18. Logarithmic plot of $J_r(t)$ vs the reduced time scales, t/a_T , with reference temperatures of 60°C (data points) and 35°C (dashed line). The corresponding $J(t)$ are curves dotted and dash-dotted lines, respectively [Plazek (1980)].

POLYISOBUTYLENE REVISITED

Polyisobutylene samples with very narrow molecular weight distributions have yet to be studied exhaustively. Some data obtained at the University of Pittsburgh indicate that some surprises are yet to be forthcoming. A low molecular weight sample ($M = 10\,700$) [Ngai, Plazek, and Bero(1993)] and one with a moderate molecular weight sample ($M = 78\,500$) [Plazek, Zheng, and Ngai (1992)] have been studied and the results have been reported. Both samples, with data covering approximately five decades of time, indicate thermorheologically simple behavior. Viscosities and temperature shift factors for $J_r(t)$ were found to agree within experimental uncertainty over a temperature range of 120°C . These results substantiate that PIB is certainly the most thermorheologically simple of all linear amorphous polymers.

However, for over 40 years it has been known that the loss tangent of PIB in the softening dispersion is uniquely distinctive. Instead of having a single nearly symmetrical peak as a function of logarithmic frequency, as do other amorphous polymers, it has been reported to display a strong shoulder on the high frequency side of the main peak; as shown in Fig. 27. Since this shoulder was specifically observed for the NBS PIB [Ferry, Grandine, and Fitzgerald (1953)] and we saw nothing to indicate its presence in the PIBs we had studied, we obtained new creep measurements on a sample of the original NBS PIB which I still had on hand. The recoverable creep compliance curves are shown in Fig. 28 at six temperatures between -74.2 and 27.3°C . Four of the six curves cover 5

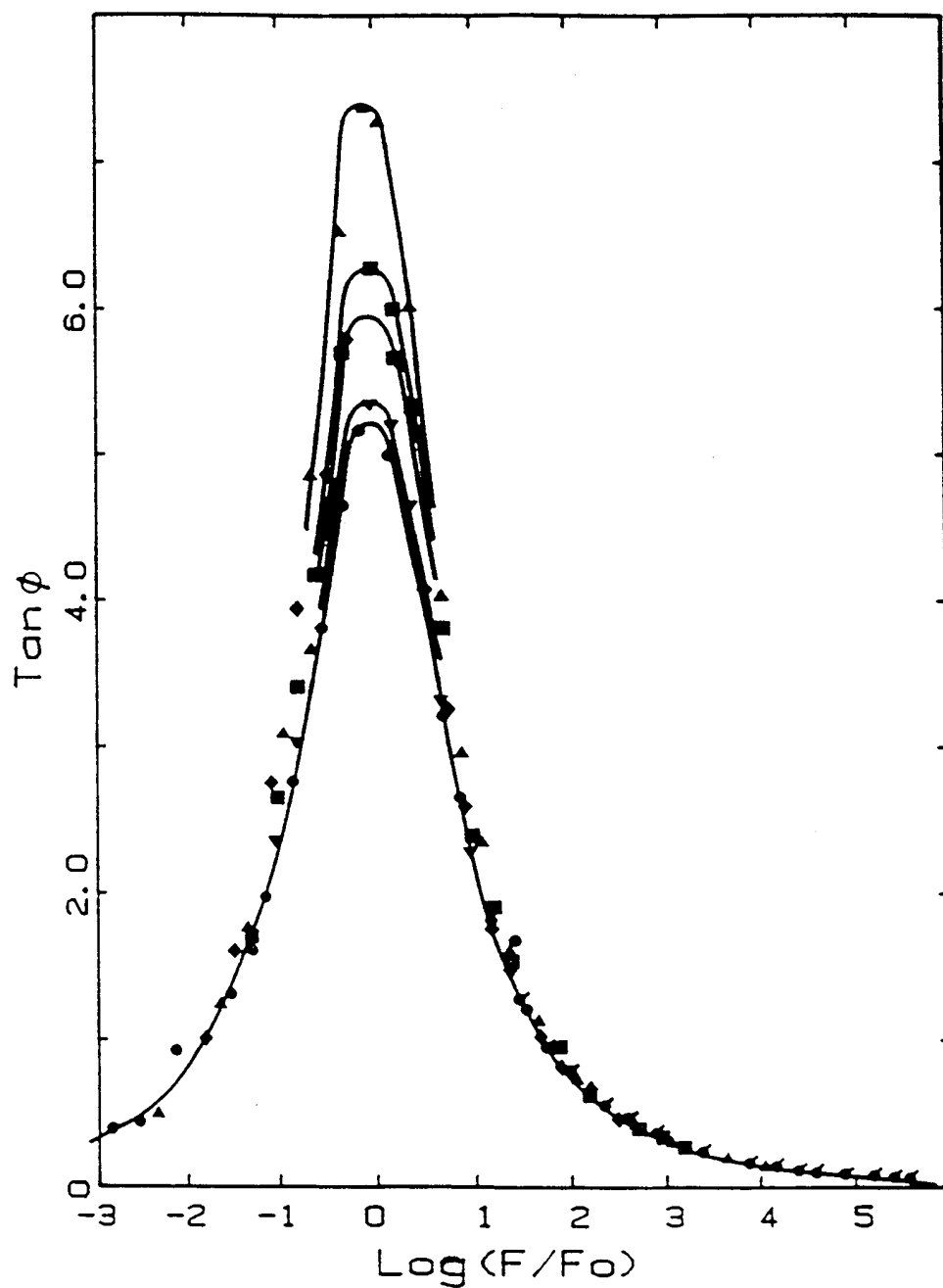


FIG. 19. $\text{Tan } \delta (= G''/G')$ of polystyrene plotted against the reduced logarithm of the frequency F/F_0 where F_0 is the frequency of the maximum. The temperatures of measurement were \bullet 86.5°, Δ 91.3°, \blacksquare 94.3°, \blacklozenge 95.8°, ∇ 98.4°, \bullet 100.7 °C. By permission [Cavaillé *et al.* (1987)].

decades of recovery time. The six curves reduced well, as seen in Fig. 29, where T_0 was chosen to be -73 °C. The retardation spectrum was determined from the reduced recoverable compliance curve and is presented in Fig. 30. Finally the components of $J^*(\omega)$ were calculated from

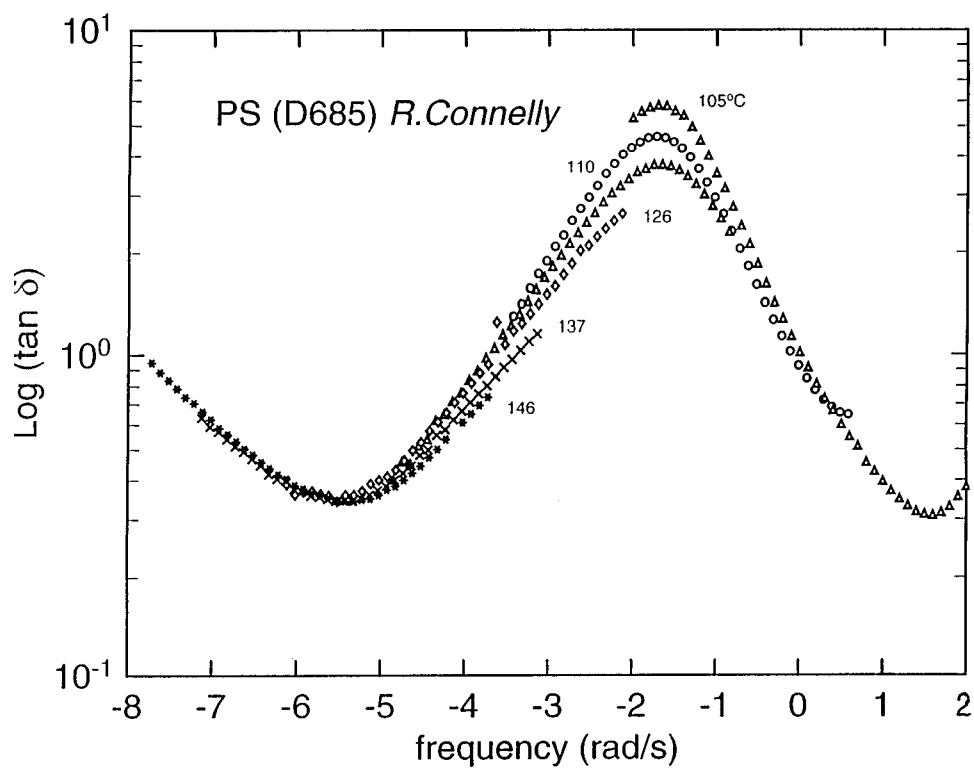


FIG. 20. Logarithm of the loss tangent for a polystyrene as a function of the logarithm of the reduced frequency, as measured by Connelly.

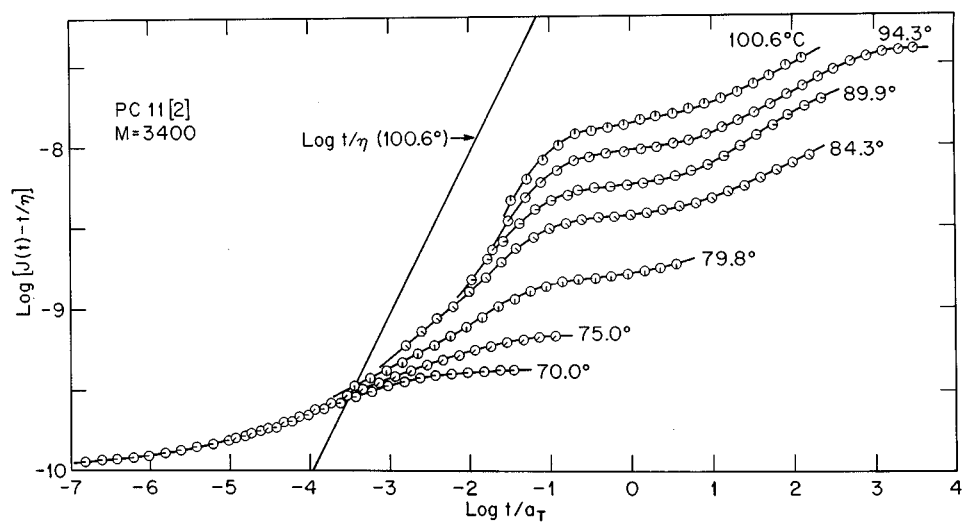


FIG. 21. Recoverable compliance for Polystyrene PC-11[2] $M = 3400$ reduced to 100°C by plotting logarithmically against the reduced time, t/a_T . The straight line is the viscous contribution to total creep at 100.6°C [Plazek and O'Rourke (1971)].

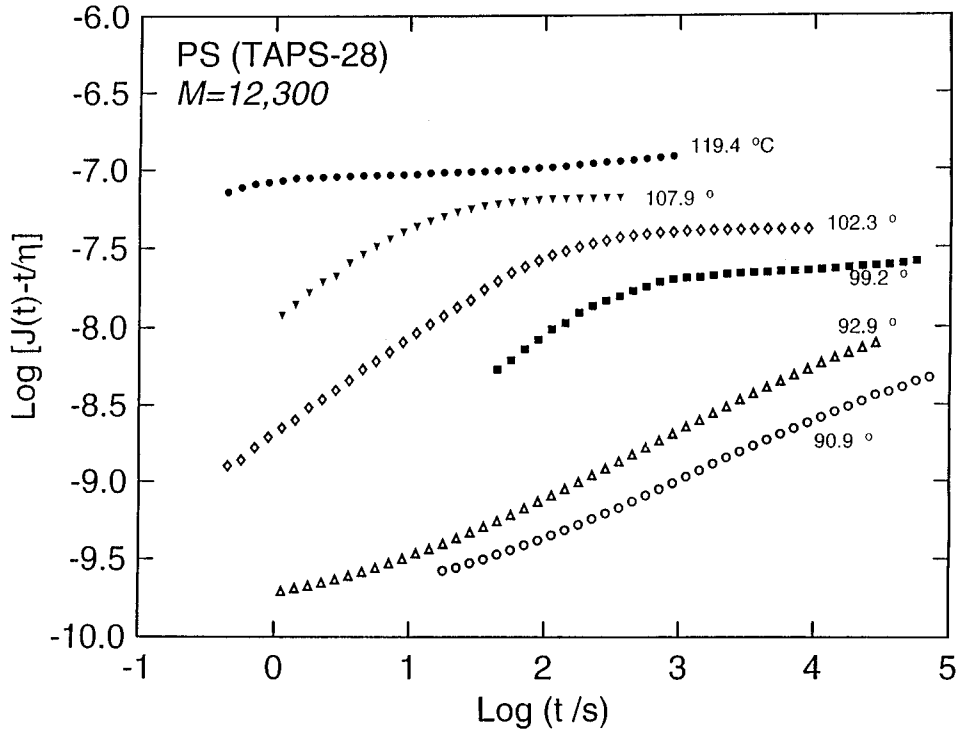


FIG. 22. Logarithm of the recoverable compliance [$J_r(t) = J(t) - t/\eta$] of a polystyrene with a molecular weight of 12 300 and a narrow distribution of chain lengths measured at six temperatures from 90.9 to 119.4 °C.

$$J' = J_g + \int_{-\infty}^{\infty} [L/(1 + \omega^2 \tau^2)] d \ln \tau$$

and

$$J'' = \int_{-\infty}^{\infty} [L\omega\tau/(1 + \omega^2 \tau^2)] d \ln \tau + 1/\omega \eta_0.$$

They are plotted logarithmically in Fig. 31 along with the $\tan \delta$ as functions of the logarithmic reduced frequency. It was surprising and puzzling to see that the $\tan \delta$ curve showed no high frequency shoulder. Although isochronal or resonance temperature scans have failed to report this low temperature shoulder or peak in $\tan \delta$; [McCrum, Read, and Williams (1967); McCall (1969)] its existence was not in doubt. Not only did Ferry, Grandine, and Fitzgerald (1953) report it, but I knew it had been observed by the Rubber Reserve Group at Mellon Institute [L. Zapas, personal communication] and by C. M. Roland at the Naval Research Laboratory [personal communication]. As a consequence, I decided to scrutinize our original unreduced curves. Slopes were determined manually and from spline-function fits (computer programs written by S. J. Orbon) to each individual curve; with excellent agreement. With these slopes and the following empirical relations [Plazek, Raghupathi, and Orbon (1979)]:

$$J'(\omega) = [1 - m(2t)]^{0.8} J_r(t) \Big|_{t = 1/\omega},$$

$$J''(\omega) = [m(\frac{2}{3}t)]^{0.8} J_r(t) + 1/\omega \eta_0 \Big|_{t = 1/\omega},$$

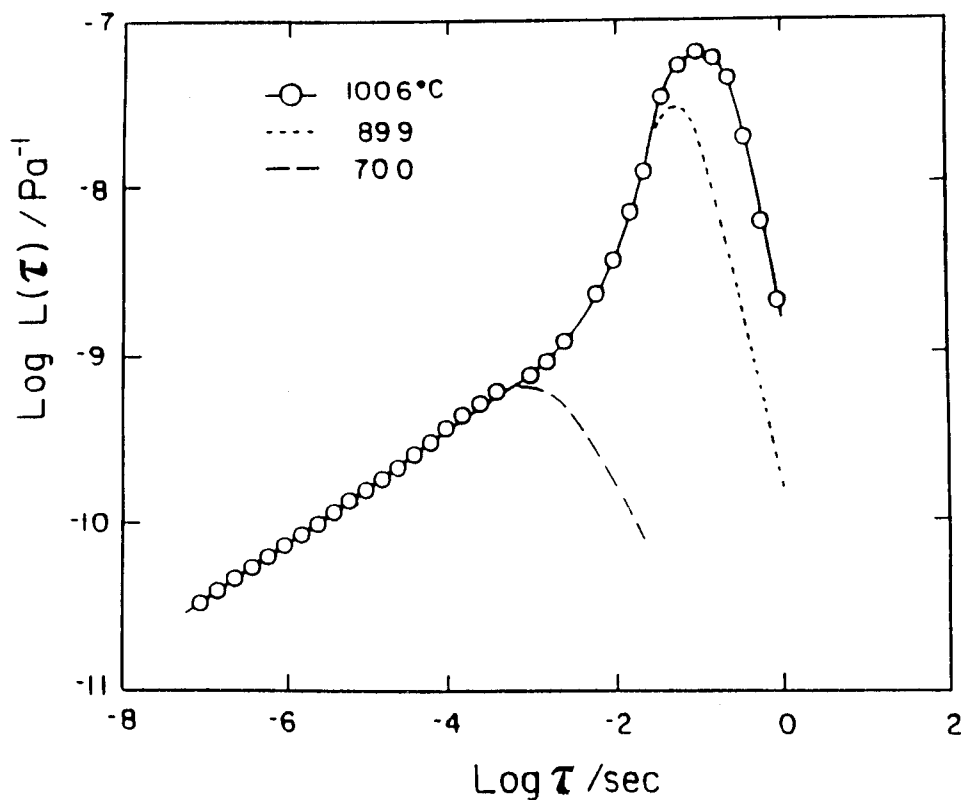


FIG. 23. Logarithm of the retardation spectrum $L(\ln \tau)$ of polystyrene PC-11[2] for three temperatures, as indicated, shifted to the reference temperature $T_0 = 100.6^\circ\text{C}$ as functions of the logarithmic reduced time scale.

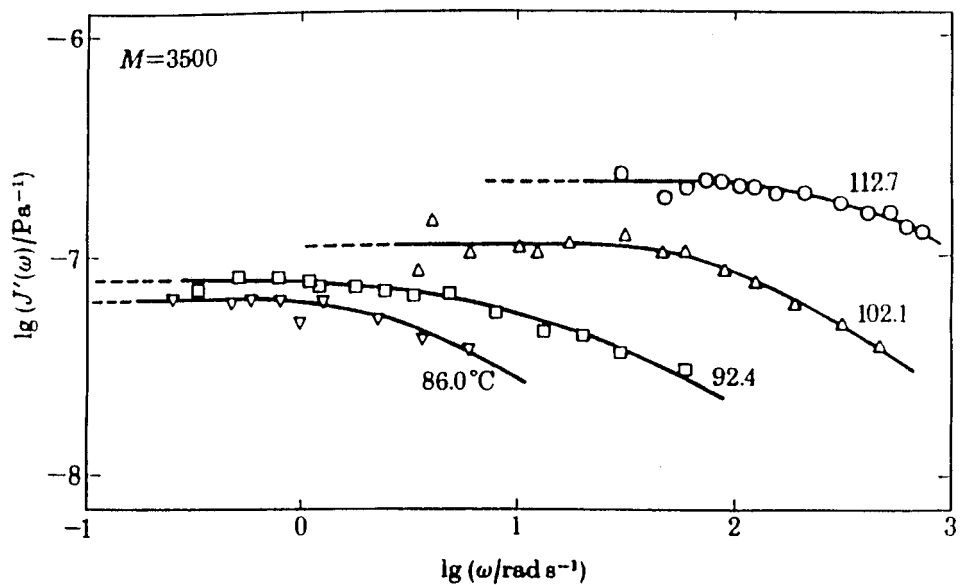


FIG. 24. The real component $J'(\omega)$ of the complex dynamic shear compliance of a polystyrene ($M = 3500$) as a function of the logarithmic frequency. By permission [Gray, Harrison, and Lamb (1976)].

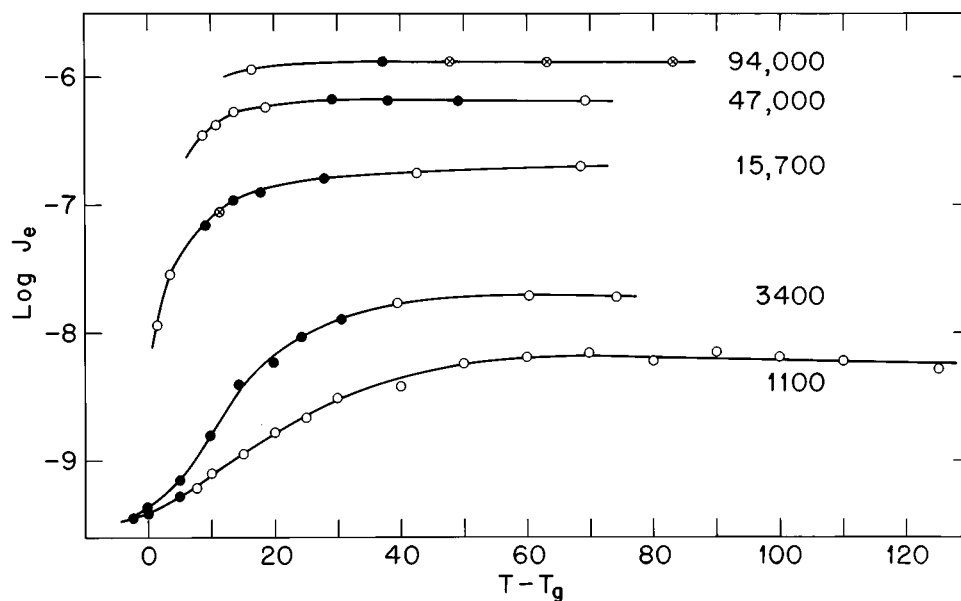


FIG. 25. The steady-state recoverable compliance, J_s , cm^2/dyn , presented semilogarithmically as a function of temperature, $T - T_g$, for polystyrenes of differing molecular weights.

where $m = d \log J_r(t) / d \log t$, the loss tangent values shown as filled symbols in Fig. 32 were obtained.

The open circle data points at -35.0°C were obtained from [Fitzgerald, Grandine, and Ferry (1953)] and the open circles and open triangles at -52.0 and -35.8°C ,

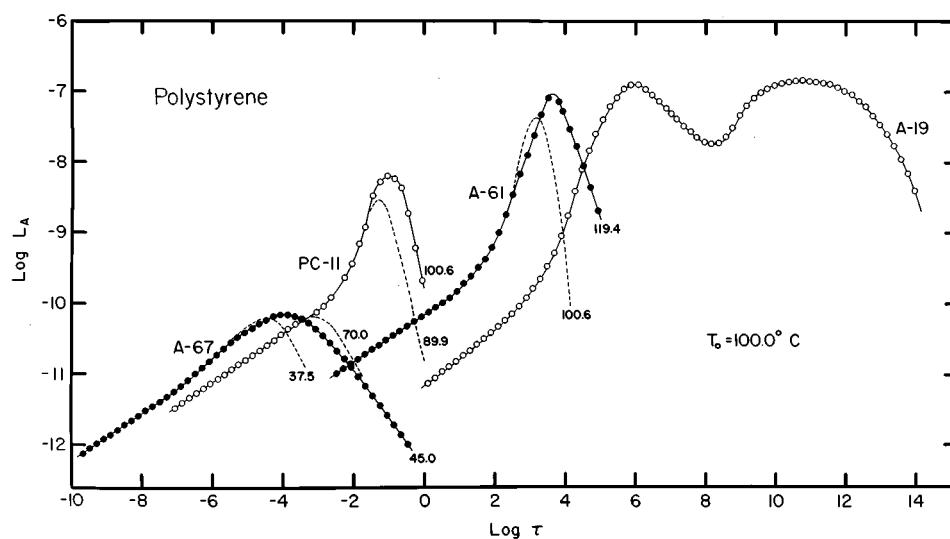


FIG. 26. Logarithmic retardation spectra L for four polystyrenes with molecular weights of 1100 (A67), 3400 (PC-11), 16 400 (A61), and 600 000 (A19) as functions of the logarithmic reduced retardation times. All of the L 's are reduced to $T_0 = 100.0^\circ\text{C}$.

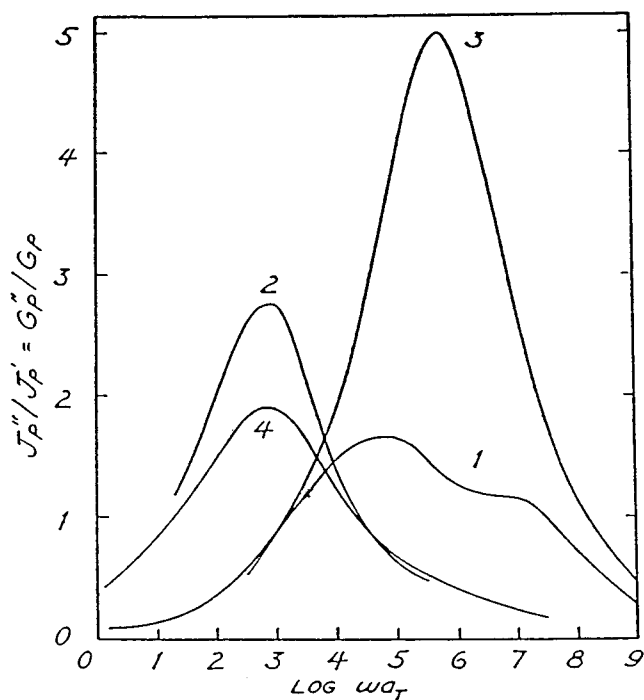


FIG. 27. Reduced loss tangents for (1) polyisobutylene, (2) polystyrene, (3) polyvinyl chloride-dimethyl thianthrene composition with 10% polymer, (4) polyvinyl chloride-dimethyl thianthrene composition with 40% polymer. Reference temperature for (1), (3), and (4), 25 °C; for (2), 125 °C. By permission [Ferry, Grandine, and Fitzgerald (1953)].

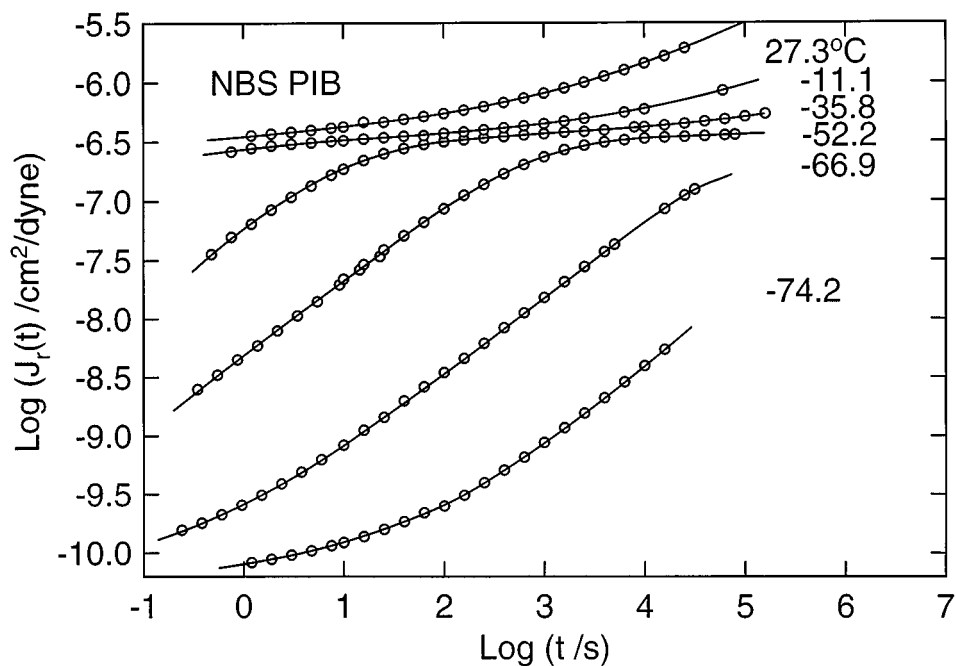


FIG. 28. Logarithmic $J_r(t)$ curves for the NBS PIB at six temperatures between -74.2 and 27.3 °C as functions of logarithmic time [Plazek *et al.* (1995)].

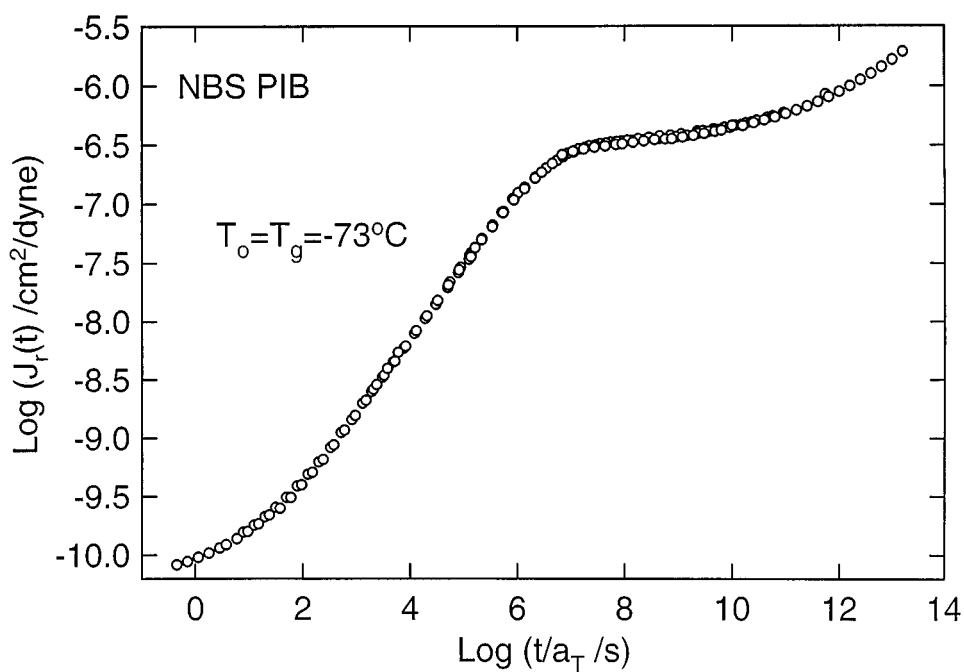


FIG. 29. NBS PIB log $J_r(t)$ curves from Fig. 28 reduced to a reference temperature of -73°C [Plazek *et al.* (1995)].

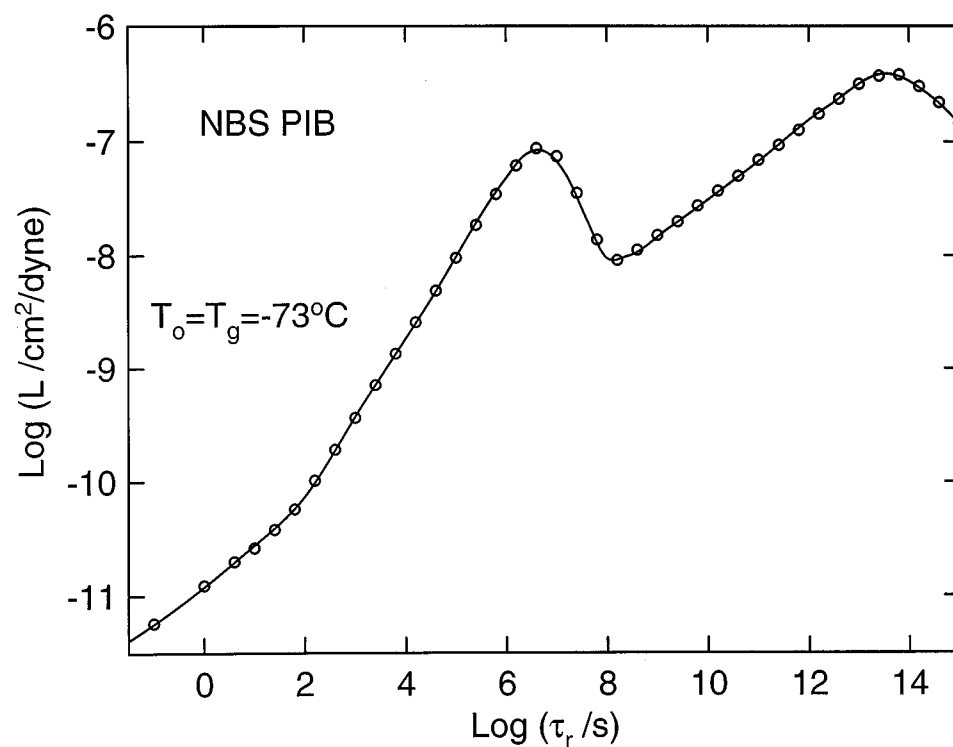


FIG. 30. The retardation spectrum $L(\ln \tau)$ for NBS PIB at -73°C determined from the reduced curve in Fig. 28 [Plazek *et al.* (1995)].

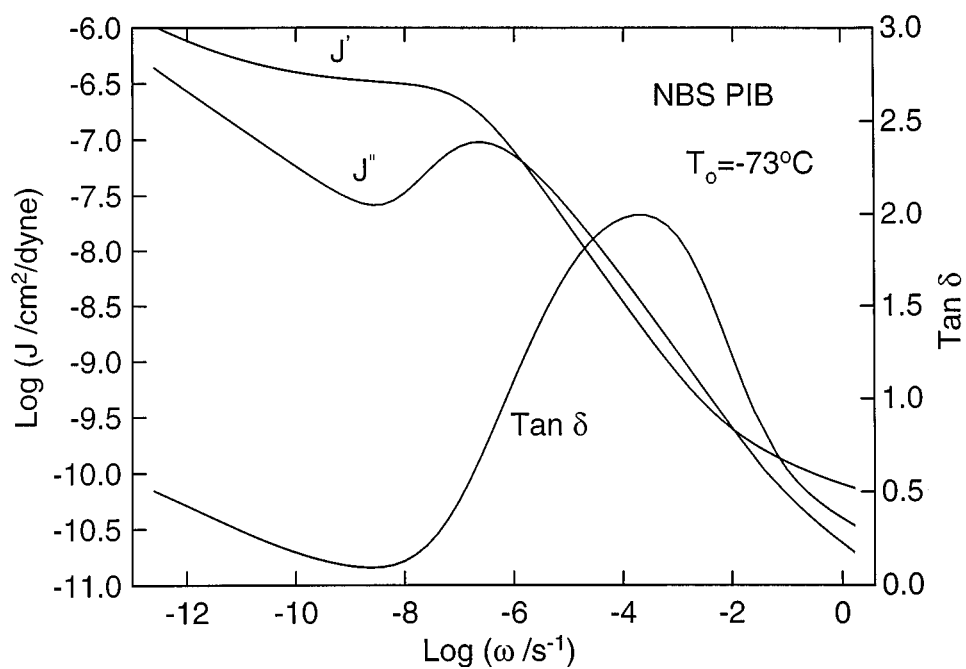


FIG. 31. The components of the dynamic complex shear compliance $J^*(\omega) = J' - iJ''$ calculated by numerical integration involving the $L(\ln \tau)$ for NBS PIB at -73°C determined from the reduced curve in Fig. 28 [Plazek *et al.* (1995)].

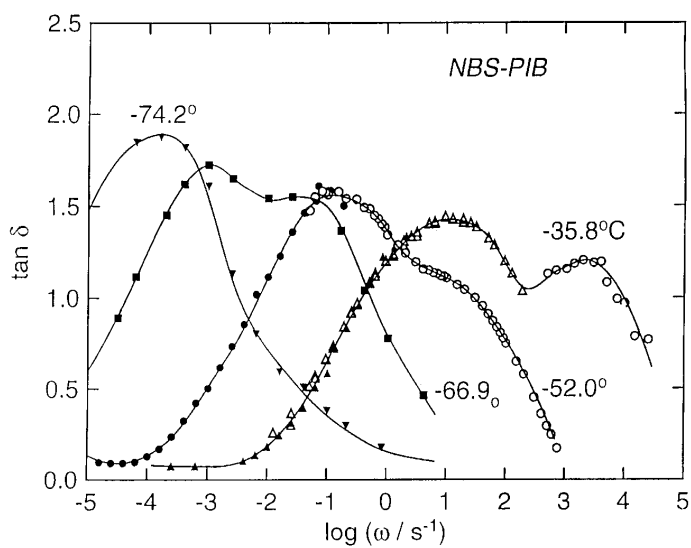


FIG. 32. The loss tangent for the NBS PIB at four temperatures as indicated. Data points originate from three separate studies as described in the text [Plazek *et al.* (1995)].

respectively, were obtained by C. M. Roland [Plazek *et al.* (1995)]. The composite data set in Fig. 31, with curves covering 5–8 decades of frequency, clearly show that the most thermorheologically simple of polymers PIB is thermorheologically complex. Two maxima in $\tan \delta$ are present at -35.8 °C. However, since the higher frequency peak arises from a group of molecular mechanisms with a stronger temperature dependence than that of the mechanisms contributing to the lower frequency peak, the higher frequency peak overtakes the lower one and merges with it with decreasing temperature. It is also clear that the subtle contributions to the recoverable compliance curves reflecting the peak or shoulder were reduced out of existence in obtaining the reduced recovery curve in Fig. 28. It has been proposed that the high frequency loss peak represents the contribution of sub-Rouse molecular modes of motion to the compliance [Ngai and Plazek (1995)].

CONCLUDING OBSERVATIONS

Although there are a number of exceptions to thermorheological simplicity the reduction process is still one of our most valuable tools for the analysis of viscoelastic data. Molecular mechanisms within related groups do have the same temperature dependence; hence reduction failure allows the identification and separation of different kinds of mechanisms.

For many years I have had the following quotation of Frederick Novalis hanging over my desk:

To become acquainted
with a truth we must
first have disbelieved it and
disputed against it.

This reluctance to the ready acceptance of new ideas certainly is not part of any Dale Carnegie course on how to win friends and influence people. As a matter of fact it leads to some confrontation and controversy (hopefully friendly in nature). I should finally like to add that the above “truth” is at best approximate and at worst temporary.

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