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Physical aging by periodic creep and interrupted creep experiments

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A newly developed ''interrupted creep'' experiment has been used to study the physical aging of a low molecular weight polystyrene, $T_g \sim 69\,°C$. The results of the new experiment are compared to those obtained from traditional ''periodic creep'' experiments. The interrupted creep experiment provides information about the viscosity, the recoverable creep compliance and the steady-state compliance, J_s, during aging. Low molecular weight polystyrene was chosen because it exhibits a steady-state compliance that is a strong function of temperature. Aging was conducted at three temperatures, 68.2, 65.7 and 61.0 °C, using both down-jump and up-jump experiments. The behavior observed in the new experiments mirrors the behavior observed in the traditional experiments. In addition, the new experiments allow the first ever determination of how J_s evolves during aging. The change of J_s with aging time was calculated using the relationship between the shift factors, obtained from the recoverable creep compliance data, and the average relaxation times, obtained from the viscosity. The advantage of the new experiment is that it provides both the short-time recoverable creep compliance information and the long-time viscous flow. By combining these contributions to the creep compliance in a simple additive fashion, one can obtain a more complete picture of how the material is behaving during aging. © *1999 American Institute of Physics.* [S0021-9606(99)70429-0]

I. INTRODUCTION

An amorphous polymer above its glass temperature, T_g, is an equilibrium or metastable liquid. As the liquid is cooled, the mobility of the material decreases. When the structural changes needed to maintain equilibrium cannot be achieved in the time scale of the experiment, the material falls out of equilibrium and becomes thermodynamically unstable and is called a glass. The glass temperature is a kinetic event and characterizes the shift from equilibrium behavior to glassy behavior. The exact value of the glass temperature is a function of the cooling rate. Since a glass is not in thermodynamic equilibrium, its physical and mechanical properties evolve with time through changes in molecular configuration. As the polymer approaches the equilibrium state there is a decrease in specific volume, enthalpy, entropy, and the rate of creep, and an increase in brittleness. In this study, the effects of aging on viscosity and the recoverable creep compliance were investigated.

During the quenching segment of a down-jump aging experiment, the viscosity shows a step change increase corresponding to the glassy volume; see solid line (a) in Fig. 1. Upon reaching the aging temperature, the viscosity continues to increase with time along the dotted line, as the volume decreases toward equilibrium density. The viscosity following an up-jump departs immediately from equilibrium along line (b) to a lower value and then decays to the new equilibrium value. The viscosity behavior observed inversely parallels the underlying changes in volume.

The changes in the dynamic mechanical properties of a polyvinyl acetate, measured after a temperature down-jump to below T_g, were first reported in 1963 by Kovacs, Stratton and Ferry.[1] In 1966, the decrease in the rate of creep of the organic compound tri-napthyl benzene was reported at temperatures below T_g.[2] Subsequently, Struik published his thesis on *Physical Aging in Amorphous Polymers and Other Materials*, in 1978,[3] wherein periodic creep compliance measurements were used to follow the effects of densification below T_g. Figure 2 is a schematic of the stress, strain and temperature history for a periodic creep down-jump experiment similar to the one used by Struik.

The periodic creep experiment consists of quenching to a temperature below T_g and applying a load at approximately equal logarithmic increments of aging time.[3] Note that there are two time scales in the experiment: the aging or elapsed time, t_e, which begins when the temperature has reached the aging temperature, T_a, and the creep time, t, which begins at the moment of loading. Creep times are performed for less than 10% of the aging time ($0.1\,t_e$) in order to insure that no appreciable aging occurs during the creep test. The time between successive creep tests generally doubles or triples, allowing sufficient time for creep-recovery. The time between measurements is necessary to insure that the strain change due to creep-recovery from one loading is negligible compared to the subsequent loading. For clarity, the unique creep measurements taken during the aging process will be referred to as individual tests or measurements. The series of measurements that characterize the material during the entire aging process will be referred to as the experiment, i.e., each

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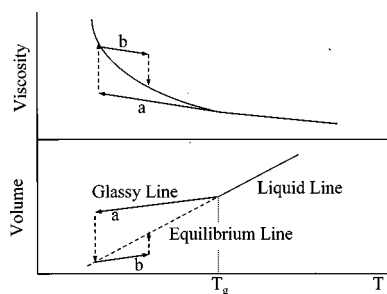[a)]Authors to whom correspondence should be addressed.

FIG. 1. Volume and viscosity behavior vs temperature during up-jump and down-jump experiments. The dashed line extending from the liquid line in the lower figure represents the equilibrium line below the glass transition. The glassy line departs from the equilibrium line at T_g. Sloped lines a and b occur during the temperature quench, and are relatively rapid ($<10^3$ sec). Vertical dashed lines are followed during aging and, depending on the temperature relative to T_g, the changes can take over 10^7 sec.

periodic creep experiment consists of a series of unique creep compliance measurements. The time-dependent response of the creep compliance to a temperature up-jump is measured in a similar fashion.

The time-dependent creep compliance can be described by the sum of ''elastic,'' retarded, and viscous contributions[4,5] as shown in Eq. (1),

$$J(t) = J_g + J_d \Psi(t) + t/\eta. \tag{1}$$

The apparent elastic response is represented by the glassy compliance, J_g, the retarded response by the normalized memory function, $\Psi(t)$, and the viscous contribution by t/η, where η is the shear viscosity coefficient. The memory function goes from $\Psi(0)=0$ to $\Psi(\infty)=1$ with $J_d=J_s - J_g$. The steady-state compliance, J_s, is defined as the long-time limiting value of $J_r(t)$ for a non-crosslinked system. The normalized memory function can also be written in terms of a distribution of retardation times, $L(\tau)$,

$$\Psi(t) = \frac{1}{J_d} \int_{-\infty}^{\infty} L(1 - e^{-t/\tau}) d \ln \tau. \tag{2}$$

Following a decrease in temperature, the creep compliance curves shift to longer times, as the aging time increases. The shift of the creep compliance curves reflects the increase in the statistically meaningful retardation times. If the only
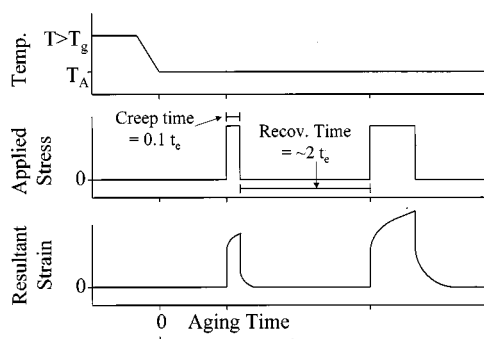

FIG. 2. Schematic of temperature history, applied stress and resulting strain for the periodic creep down-jump experiment. The creep time is the length of time that the load is applied and the recovery time is the length of time between subsequent creep measurements.

effect of aging were a shift of the entire spectrum to longer times, without a change in spectral shape and magnitude, creep curves taken at different aging times would be superposable by only a horizontal time-scale shift, $\log a_e$. However, the reduction of aging curves generally involves an empirical vertical shift, $\log b_e$, which is small, coupled with the horizontal shift. Following a temperature down-jump, the vertical shift is usually negative, although Struik has reported two cases for positive shifts.[3] It is our hypothesis that the vertical shifts are a manifestation of an underlying change in J_s with aging.

Although the periodic creep experiments are used to characterize the changes that occur during physical aging, they do not allow one to distinguish information concerning the changes in viscosity or the steady-state compliance. To the best of our knowledge, the evolution of either of these properties during aging below T_g has not been previously measured for polymers. In particular, the value of the steady-state compliance cannot be measured in traditional creep experiments as a function of aging time because the time to reach steady-state is longer than the time to reach equilibrium density such that only the equilibrium value of J_s can be observed. In addition, the act of measuring the equilibrium value of J_s would require creeping below T_g for a period of several days, weeks or longer to reach steady-state. In this work, we circumvent these problems by applying a technique reported by Leaderman, Smith and Jones[6] to our aging experiments.

Leaderman *et al.* analyzed several low molecular weight polyisobutylene (PIB) samples at temperatures below 0 °C.[6] At these low temperatures, the time to reach steady-state was long enough that Leaderman *et al.* adopted the following procedure: a load was applied at 0 °C until steady-state was known to have been reached. The temperature was then lowered while maintaining the torque, to several measurement temperatures. At each temperature, enough time was allowed for the sample to reach thermal equilibrium before monitoring the angular velocity, which yielded the viscosity. Leaderman *et al.* also obtained recoverable creep compliance data above T_g in a related fashion except that only one measurement was made following each quench. By following a similar procedure, we believe it is possible to monitor aging using successive creep-recovery measurements. Since the recoverable creep compliance often provides a more complete picture of the material,[7] the ability to obtain accurate creep-recovery data during aging can advance the understanding of how a material approaches equilibrium. In addition, it will be possible to monitor the viscosity versus aging time.

The new interrupted creep experiment which we propose consists of applying a constant load above T_g for a time long enough to reach steady-state. Once in steady-state, the material is quenched to the aging temperature, T_a, while maintaining the constant load. Successive creep-recovery measurements are made at logarithmic increments of time. A schematic of the interrupted creep experiment for a temperature down-jump is shown in Fig. 3. The rate of creep is monitored until the first creep-recovery measurement, when the load is removed. After the first test, the load is reapplied

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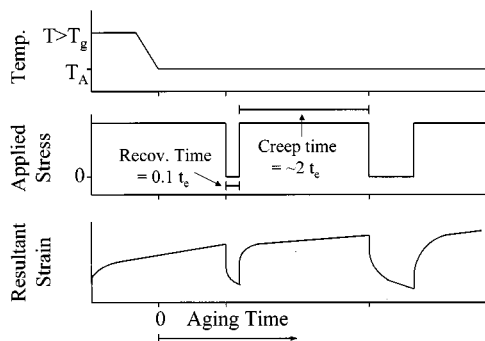Aging and interrupted creep experiments   2237

FIG. 3. Schematic of temperature history, applied stress and resulting strain for interrupted creep down-jump experiment. The creep time is the time that the torque is applied between the sequential creep-recovery measurements, each of which is of 0.1 t_e duration.

FIG. 4. Log J_s as a function of temperature for a 3400 molecular weight polystyrene (Ref. 10). Solid line is to guide the eye only.

and the creep rate is again monitored to insure that adequate time has passed before the next measurement. The length of each creep-recovery measurement, and the time between subsequent measurements, follows the procedure described above for the periodic creep experiments.

The new interrupted creep experiment is based on the assumption that once a material reaches steady-state creep, a change in temperature will not disturb this condition if J_s is independent of temperature. For materials where this assumption is valid, such as 1,3,5-tri-α-naphthylbenzene (TαNB), aging experiments performed in this laboratory[8] have indicated that steady-state is maintained after temperature down-jumps. The work by Leaderman et al. on PIB[6] also supports this hypothesis.

Even for the case where J_s is a strong function of temperature, the new experiment is expected to provide the viscosity and $J_r(t)$. The viscosity can be measured as a function of aging time because the rate of viscous deformation accumulating in the quasi-steady-state regime will be orders of magnitude larger than the rate of recoverable deformation. Consequently, the evolution of J_s with aging time, t_e, can be calculated through the relation,[9]

$$\log a_e = \log \frac{\langle \tau \rangle}{\langle \tau_{\text{ref}} \rangle} = \log \frac{\eta J_s}{\eta_{\text{ref}} J_{s_{\text{ref}}}}, \qquad (3)$$

where a_e are the shift-factors used to reduce the recovery aging data, $\langle \tau \rangle$ is the average relaxation time at a specific t_e and η is the viscosity.

In this work, the physical aging behavior of a low molecular weight polystyrene (PS) is examined using both periodic creep experiments and the new interrupted creep experiments at three aging temperatures. This material was chosen because low molecular weight polystyrene has a J_s that is a strong function of temperature.[10] A plot of J_s vs temperature is shown in Fig. 4 for a polystyrene of similar molecular weight.

II. EXPERIMENT

A. Material

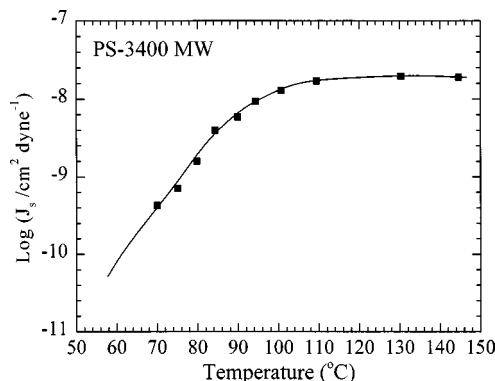The material studied was a low molecular weight polystyrene designated as PC-4000[4]. The sample was the fourth

cut from a fractionation of a narrow distribution anionically polymerized sample. The molecular weight was determined to be 3300 g/mol by analytical GPC using THF as the column solvent. The polydispersity, M_w/M_n, was calculated to be 1.09.

The glass temperature of PC-4000[4] was determined as a function of *cooling* rate by a Perkin Elmer DSC 7 using a refrigeration unit and a nitrogen purge. T_g at cooling rates of 3, 5 and 10 °C/min were calculated to be 71.0, 72.2 and 74.8 °C, respectively. Using the WLF equation,[11] T_g for a cooling rate of 0.2 °C was determined to be 68.7 °C with $C_1 = 13.46$, $C_2 = 28.90$ and $T_{\text{ref}} = 51.4$ °C.[10] The T_g determined at a cooling rate of 0.2 °C/min will be referred to hereafter as the glass temperature of our low molecular weight polystyrene. The density of our polystyrene was determined by a correlation reported by Fox and Loshaek,[12]

$$1/\rho = 0.767 + 5.5 \times 10^{-4} T + 643 \times 10^{-4} T/M, \qquad (4)$$

with $M = 3300$ and T in Kelvin, and is equal to 1.04 g/cm^3 at 68.2 °C. The density is used in determining the sample coefficient as a function of temperature.

B. Creep and recoverable creep compliance studies

Creep and recoverable creep compliance studies were performed in a magnetic-bearing torsional creep apparatus that has been described elsewhere.[13] Two PC-4000[4] samples of 26±2 mg mass were used for all measurements.

TABLE I. Time and temperature history of aging experiments.

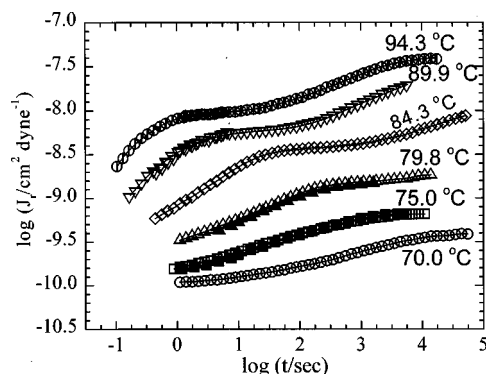|	Temp. jump (°C)	No. of tests	Sample no.	Longest t_e (s)
Down-jumps				
Periodic	84.6→68.2	5	1	162 000
Periodic	73.4→68.2	4	2	235 000
Interrupted	73.7→68.2	4	1	88 300
Periodic	68.2→65.6	6	2	518 000
Interrupted	68.2→65.7	6	1	946 000
Periodic	94.6→61.0	6	1	845 000
Up-jumps				
Periodic	65.6→68.2	5	2	268 000
Interrupted	65.7→68.2	6	1	167 000

FIG. 5. Double log plot of the recoverable creep compliance of PC-4000[4] (filled symbols) and a 3400 molecular weight PS PC-11[2] (open symbols) (Ref. 10).

Moisture was removed from the polymer by drying the material *in situ* under vacuum ($\sim 2 \times 10^{-2}$ Torr) at a temperature slightly above T_g. All experiments were performed isothermally under a nitrogen atmosphere in a sealed sample chamber. The time and temperature history of the experiments performed are shown in Table I.

The viscosity is determined using the following relationship,

$$\frac{1}{\eta} = \frac{k\dot{\Theta}}{\tau}, \tag{5}$$

where k is the sample coefficient, $\dot{\Theta}$ is the angular deformation in radians/sec, and τ is the applied torque in dyne cm.

III. RESULTS

The recoverable creep compliance and the viscosity for PC-4000[4] were measured at several temperatures above T_g. The results are shown in Figs. 5 and 6, along with data for a PS of molecular weight 3400.[10] There is reasonable agreement between the recoverable compliance values of both samples. The second dispersion shown in this figure is a result of a high molecular weight tail[10] and can be ignored for the purposes of determining the value of the steady-state compliance of the principal species. The viscosity behavior also exhibits good agreement between both sets of data.
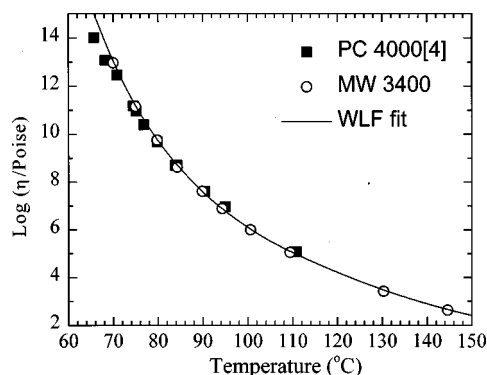

FIG. 6. Viscosity of low molecular weight polystyrenes with a WLF fit using parameters determined in Ref. 10 and reported in Sec. II. Filled symbols are PC-4000[4], open symbols are PC-11[2] (Ref. 10).
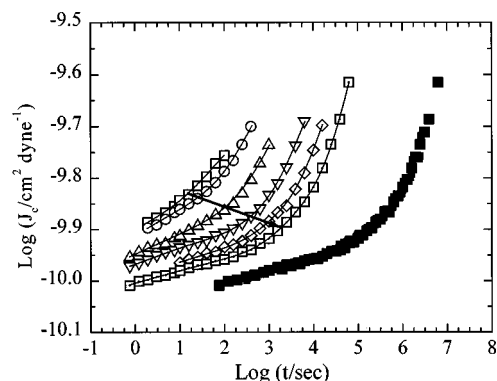

FIG. 7. Plot of $\log J_c(t)$ vs $\log t$ for a periodic creep down-jump experiment (94.6 to 61.0 °C) for six aging times: $t_e = 1800$ ($\square$), 5460 ($\bigcirc$), 17 300 ($\triangle$), 92 100 ($\triangledown$), 263 000 ($\diamond$) and 845 000 sec ($\boxdot$). Reduced curve is shown by filled symbols and is shifted by two log units. Arrow indicates direction of shifting needed for reduction.

The time-dependent shear creep compliance, $J_c(t)$, for the down-jump experiment from 94.6 to 61.0 °C is shown in Fig. 7. This figure shows a double log plot of $J_c(t)$ vs t at six different aging times, t_e. The effect of physical aging on the creep compliance is a shifting of the creep curves to longer times, coupled with a small vertical shift, as indicated by the arrow. The reduced curve is shown in the figure by the solid symbols, offset two decades to longer times. The shift factors used in the reduction were calculated by shifting the curves by hand. The reference curve used for the reduction of this data was the longest aging time curve, $t_e = 845\,000$ sec. Similar behavior is observed for all the periodic creep down-jump experiments, though in several of the experiments the total horizontal shift was less than one decade in time, and in these experiments vertical shifts could not be accurately determined. For example, Fig. 8 shows the creep compliance behavior for the temperature down-jump from 84.6 to 68.2 °C.

In addition, the viscous contributions to the total creep compliance are shown in Fig. 8 as the four straight lines.
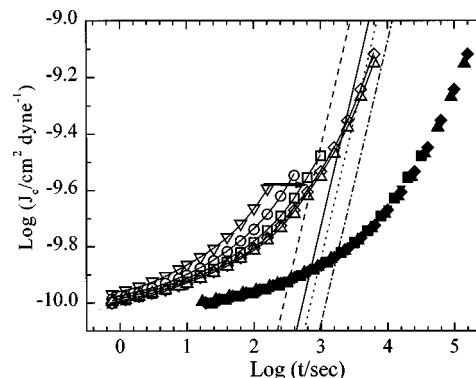

FIG. 8. Plot of $\log J_c(t)$ vs $\log t$, for a periodic creep down-jump experiment (84.6 to 68.2 °C) for five aging times: $t_e = 1800$ ($\triangledown$), 6180 ($\bigcirc$), 21 000 ($\square$), 73 300 ($\diamond$), and 162 000 sec ($\triangle$). Lines are viscous contribution lines from an interrupted creep experiment following a similar temperature history: $t_e = 1740$ (dashed line), 6600 (solid line), 16 800 (dotted line), and 88 400 sec (dot-dashed line). Reduced curve is shown by filled symbols and is shifted by two log units. Arrow indicates direction of shifting needed for reduction.
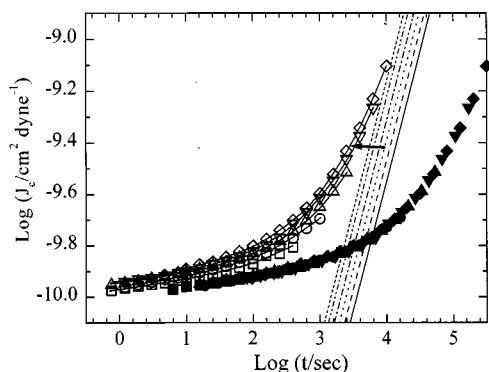
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FIG. 9. Plot of log $J_c(t)$ vs log t, for a periodic creep up-jump experiment (65.6 to 68.2 °C) for five aging times: $t_e = 4950$ (□), 16 000 (○), 43 600 (△), 106 000 (▽), and 268 000 sec (◇). Lines are viscous contribution lines from an interrupted creep experiment following a similar temperature history: $t_e = 3180$ (solid line), 8700 (dashed line), 19 500 (dotted line), 40 900 (dash-dot line), 82 800 (dash-dot-dot line) and 167 000 sec (small dashed line). Reduced curve is shown by filled symbols and is shifted by 1.5 log units. Arrow indicates direction of shifting needed for reduction.

These ''t/η'' lines were obtained from an interrupted creep experiment following a similar temperature history and demonstrate that even at the longest times the contribution due to viscous flow is only a fraction of the total creep compliance.

The up-jump experiments produced similar data except that the individual creep curves shift to shorter times as the aging time increases. This is shown in Fig. 9 for the periodic creep experiment from 65.6 to 68.2 °C. Also shown are the viscous contribution lines from an interrupted creep experiment for the same temperature jump.

The results of the interrupted creep down-jump experiment from 68.2 to 65.7 °C are shown in Fig. 10. The recoverable creep compliance, $J_r(t)$, shifts to longer times during the experiment, similar to the results of the periodic creep down-jump experiments.

In addition to the shift factors associated with aging, the evolution of viscosity with aging has been determined from
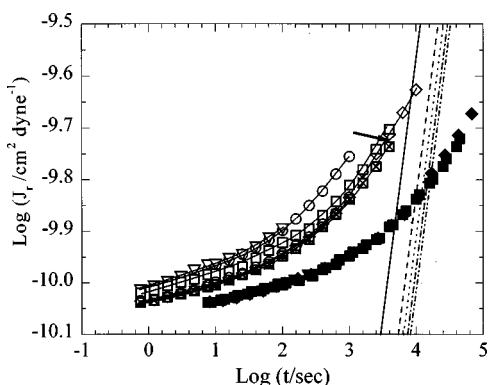

FIG. 11. Log viscosity vs log aging time, t_e, for three interrupted creep experiments. The sequence of the experiments is the 73.7 to 68.2 °C down-jump (○), next the 68.2 to 65.7 °C down-jump (□) and finally the 65.7 to 68.2 °C up-jump (■).

the interrupted creep experiments and is shown in Fig. 11. The sequence in which the experiments were performed is indicated in the figure by the numbers next to the temperature history. As expected, the viscosity increases during a down-jump experiment and decreases during an up-jump experiment.

Figure 12 is a plot of the evolution of viscosity and shift factors vs aging time for the temperature down-jump experiments to $T_a = 68.2$ °C. The evolution of viscosity with aging falls on the same curve as the shift factors associated with the periodic creep experiment, but the shift factors from the interrupted creep experiments deviate at large aging times. This behavior is also seen with the up-jump shift-factors as shown in Fig. 13.

The change of J_s with aging was calculated from Eq. (3) using the values of log a_e and log η calculated from the interrupted creep experiments. The reference values for the viscosity and steady-state compliance at equilibrium density were, $10^{13.16}$ poise and $10^{-9.52}$ cm^2/dyne, respectively. The equilibrium viscosity values were calculated from actual

FIG. 10. Plot of log $J_r(t)$ vs log t, for an interrupted creep down-jump experiment (68.2 to 65.7 °C) for six aging times: $t_e = 2100$ (▽), 5490 (○), 94 800 (□), 242 000 (◇), 527 000 (⊙), and 946 000 sec (⊠). Lines are viscous contribution lines from the same interrupted creep experiment: $t_e = 5490$ (solid line), 94 800 (dashed line), 242 000 (dotted line), 527 000 (dash-dot line), and 946 000 sec (dash-dot-dot line). Reduced curve is shown by filled symbols and is shifted by one log unit. Arrow indicates direction of shifting needed for reduction.
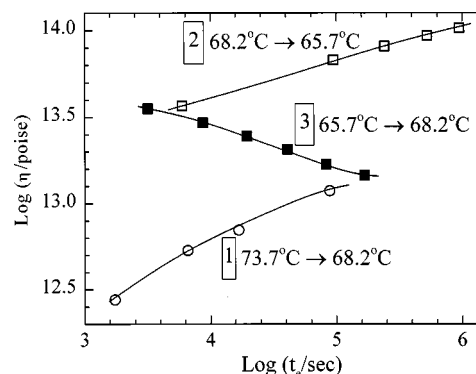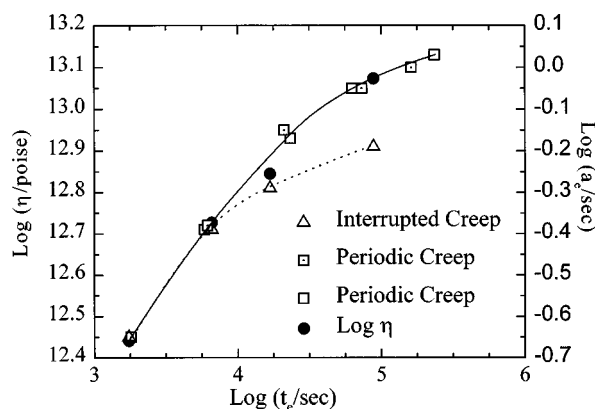

FIG. 12. Shift factors and viscosity vs log t_e for PC-4000[4] during the temperature down-jump experiments to 68.2 °C. Initial temperatures are in Table I. The squares (□,⊡) are two separate periodic creep down-jump experiments, while the viscosity (●) and interrupted creep shift factors (△) were determined during the same interrupted creep down-jump experiment. The interrupted creep data were shifted by a factor of −0.19 to allow the overlap of the short time data. This allows a clearer picture of the difference in behavior observed by the new interrupted creep experiment.
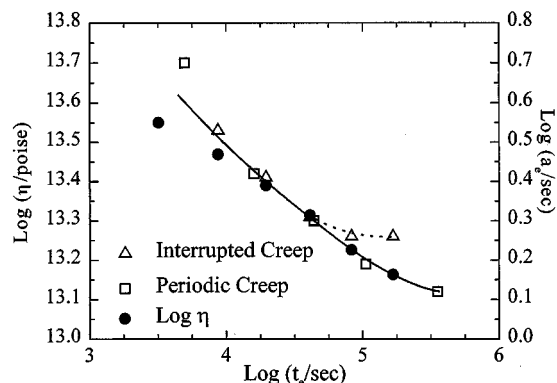
FIG. 13. Shift factors and viscosity vs log t_e for PC-4000[4] during temperature up-jump experiments from 65.7 to 68.2 °C. The squares (□) are shift factors from the periodic creep up-jump experiment, while the viscosity (●) and interrupted creep shift factors (△) were determined during the same interrupted creep up-jump experiment. The interrupted creep data were shifted by 0.12 and 0.26 for the periodic and interrupted experiments, respectively, to allow the overlap of the short time data.

measurements and extrapolation of the measured viscosity values to the aging temperature. The steady-state creep compliance at equilibrium density was calculated by extrapolating to the aging temperature from Fig. 4. A double log plot of J_s vs aging time for the temperature down-jump from 73.7 to 68.2 °C is shown in Fig. 14. For the down-jump, J_s decreases during aging. The opposite behavior is observed for the temperature up-jump experiment from 65.7 to 68.2 °C as shown in Fig. 15. The small change in J_s in Fig. 15 results from the small temperature jump used in the experiment.

IV. DISCUSSION

For the TαNB data obtained in this laboratory,[8] reduction of the recoverable creep compliance obtained as a function of aging time using the interrupted creep experiment was accomplished without a vertical shift. In that work, we also showed that the shift factor values from the interrupted creep experiments and the periodic creep experiments had the same dependence on aging time as the viscosity. These results are presumably due to the fact that J_s for TαNB is independent of temperature.
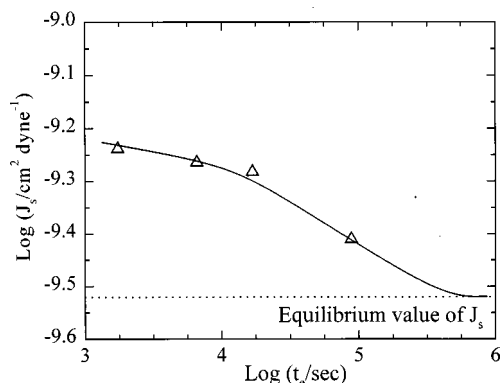

FIG. 14. Log J_s vs log aging time for the interrupted creep down-jump experiment from 73.7 to 68.2 °C. Line is to guide the eye only and does not represent a statistical fit to the data.
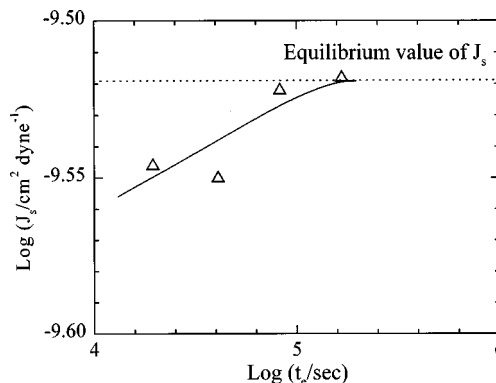

FIG. 15. Log J_s vs log aging time for the interrupted creep up-jump experiment from 65.7 to 68.2 °C. Line is to guide the eye only and does not represent a statistical fit to the data.

On the other hand, in this work on low molecular weight polystyrene, we show that the shift factors from periodic and interrupted creep experiments do not have the same dependence on aging time as the viscosity, as shown in Figs. 12 and 13. We attribute the difference to be due to the change in J_s during aging for our low molecular weight polystyrene. The periodic and interrupted creep experiments probe mechanisms operating at different time scales, which results in the change in J_s only being observed in the interrupted creep experiment. The interrupted creep experiment starts from the long-time behavior where J_s is the dominating influence. This results in a subtle, but detectable, change in the shape of the compliance curves. The periodic creep measurements start from the short-time behavior where the influence of J_s is minimal. For our low molecular weight polystyrene, for an identical temperature jump, the same change in J_s occurs regardless of the experiment performed. Since the periodic creep experiment is starting from the short-time behavior, a change in the limiting long-time behavior, J_s, cannot be observed.

We suggested earlier that the absence of vertical shifts in the TαNB was due to its temperature independent J_s. Conversely, the polystyrene was expected to need vertical shifts to reduce the recoverable creep compliance data obtained at various aging times. The experimental evidence at lower temperatures indicated that a vertical shift was required; however, reduction at 68.2 °C was accomplished without a vertical shift. The most likely explanation for the ability of the curves to be superposed with only a horizontal shift is that the vertical shift is so small that it falls within the experimental error of our measurements at 68.2 °C. The error associated with curves of the same aging experiment was calculated to be approximately 2%. The vertical shift factors calculated for the periodic creep down-jump experiment to 61.0 °C are the largest shift factors we observed, and only range from $\log b_e = 0.013$ to 0.065. Because the horizontal shifts necessary for reduction at 68.2 °C were less than one decade, it is impossible to accurately measure the vertical shifts for these experiments.

In the periodic creep experiments, the behavior of J_s cannot be detected. While it is possible that J_s changes rapidly with temperature above T_g, the fact that J_s is linked to

the shift factors means that the behavior below T_g is closely tied to the evolution of the recoverable compliance with aging. Because the shift factors associated with the viscous flow during aging are identical to the shift factors from creep, the recoverable creep compliance obtained from the new interrupted creep experiment can yield more accurate information about the true mechanisms occurring during aging.

V. CONCLUSION

Two experimental techniques have been used to measure physical aging on a low molecular weight polystyrene sample. Good agreement is obtained between the conventional time-dependent creep compliance and the new time-dependent recoverable compliance results. In addition, the ability to monitor the evolution of viscosity during aging allows a calculation of the change in J_s with aging time. It is our hypothesis that this change in J_s is the fundamental reason behind the vertical shifts that are frequently necessary to reduce data taken during aging below T_g. With this new experiment, it will be possible to test this hypothesis. Additional evidence for the evolution of J_s was observed in plots comparing the shift factors for periodic creep, shift factors for interrupted creep and the evolution of viscosity during aging. The advantage of the interrupted creep experiments is that they provide both the short-time recovery information and the long-time viscous flow data. These additive contributions to the creep compliance show a more complete picture of how the material is behaving during aging.

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