TABLE II
T_g's (°C) AND $\Delta\alpha$'s (°C^{-1}) FOR STEREOREGULAR POLY(ALKYL METHACRYLATES)

Polymer	T_g (syndio)[a]	T_g (iso)[b]	$10^4\Delta\alpha$ (syndio)[a]	$10^4\Delta\alpha$ (iso)[a]	$10^4\Delta\alpha$ (conventional)
Methyl	160	43	2.6	3.6	2.45, 3.05[d]
Ethyl	120	8	2.8	4.0	2.65,[d] 3.0[c]
Isopropyl	139	27	2.7	3.7	
Butyl	88	−24	3.0	4.4	2.3,[d] 3.4[c]
Isobutyl	120	8	2.8	3.9	2.4[d]
Cyclohexyl	163	51	2.6	3.5	

[a] Estimated, see text. [b] See ref 3. [c] See ref 22. [d] See ref 25.

It is tempting to propose that the same numerical relationship between the T_g's of the syndiotactic and isotactic isomers would also hold for the poly(2-chloroacrylates) inasmuch as the van der Waals radius of the chloride radical is very close to that of the methyl group. However, it is known that the T_g's of conventional 2-chloroacrylates are higher than those of conventional methacrylates.[28] This is probably due to the strong intermolecular forces introduced by the presence of the polar chloride groups. No data are as yet available concerning the effect of stereoregularity on the T_g's of the chloroacrylates, or of other 2-substituted acrylate polymers.

Finally, it is interesting to note that the constancy of $T_g\Delta\alpha$ in the methacrylates implies that the pressure dependence of T_g should not be a function of tacticity, at least in PMMA. This is because it has been experimentally shown that the change in heat capacity at T_g, ΔC_p is independent of tacticity[29] and thus, using the equation[30]

$$\frac{dT_g}{dP} \simeq \frac{T_g V \Delta\alpha}{\Delta C_p} \tag{5}$$

and the fact that the specific volumes at the respective T_g's are almost identical,[23] it follows that dT_g/dP is similarly independent.

Conclusions

1. This paper has drawn attention to the correlations that exist between the glass transition temperatures, steric configuration and side-chain structure in mono- and disubstituted vinyl polymers.

2. The Simha–Boyer universal values for $T_g\Delta\alpha$ appear to hold, regardless of tacticity, for PMMA, and this in turn implies constancy in V_o, the Gibbs–DiMarzio unoccupied volume, at T_g for these polymers.

3. If we assume that the effect of tacticity on T_g in the poly(alkyl methacrylate) series is strictly an intramolecular effect, then it may be shown that the differences in T_g (for totally syndio- and isotactic polymers) is constant for the series and may be predicted.

4. It is suggested that this analysis will hold for other disubstituted vinyl polymers, and that major differences in T_g should be found, for example, for the various tactic poly-2-chloroacrylates.

Acknowledgments. This work was supported in part by the Petroleum Research Foundation (W. J. MacK.) and by AFOSR(SRC)-OAR, USAF, Grant 68-1434 (F. E. K.).

---

(28) E. A. W. Hoff, D. W. Robinson, and A. H. Willbourn, *J. Polym. Sci.*, **18**, 161 (1955).

(29) J. M. O'Reilly, H. E. Bair, and F. E. Karasz, *Bull. Amer. Phys. Soc.*, **9**, 285 (1964).

(30) J. M. O'Reilly in "Modern Aspects of the Vitreous State," Vol. III, J. D. MacKenzie, Ed., Butterworth and Co., Ltd., London, 1964.

Temperature and Stress Dependence of Creep in an Acrylonitrile–Butadiene–Styrene Polymer

Robert S. Moore and Chester Gieniewski

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey 07974.

Received August 6, 1968

ABSTRACT: Tensile creep measurements were carried out on a commercial acrylonitrile–butadiene–styrene (ABS) polymer over a temperature range from 40 to 100° at stress levels from 0.6 to 1.8 × 10^8 dyn/cm^2. Experiments were conducted in a prototype of an apparatus designed to be compatible with digital acquisition systems. Analysis of the data indicated that application of the time–temperature superposition principle was of limited value due to the use of test temperatures near and below the effective glass transition temperature of the acrylonitrile–styrene component of the polymer. A strong stress dependence of the compliance was observed, even at relatively short times after loading. This was analyzed in terms of a model in which the height of the potential energy barrier to motion of the molecular flow unit is lowered by the application of stress. From this analysis the apparent volume of the flow unit was found to range from 8 to 13 Å^3 depending on the temperature and the time chosen for analysis. The slight time dependence indicated that at relatively short times the apparent size of the flow unit is smaller, but rapidly tends toward a somewhat larger asymptotic value. Analysis of the temperature dependence of the tensile viscosity and the temperature dependence of the stress required to produce a characteristic isochronal response indicated that the effective T_g of the acrylonitrile–styrene phase is about 85°. The stress dependence of the glass transition temperature is considered as well as the limitations involved in extrapolation of experimental data to long times and high stress levels.

Most analyses of the stress dependence of creep in acrylonitrile–butadiene–styrene (ABS) polymers have been carried out using empirical equations to describe the creep response. These suffer the disadvantage of not providing insight into the nature of the stress dependence, and, moreover, they usually

TABLE I: CHARACTERISTICS OF THE ABS POLYMER (SEE REF 2)

M_v	% composition			
	Additives	Acrylonitrile	Butadiene	Styrene
1.21×10^5	4.1	23.1	18.0	54.8
			Acrylonitrile–styrene phase	
		29.7		70.3
			Graft phase	
		13.2	55.7	31.1

% phase present			
Additives	Free rubber	Styrene–acrylonitrile	Graft and/or cross-linked rubber
4.5	1.7	65.6	28.2

fail in attempting to describe the dependence on temperature. A somewhat different analysis is given below for an ABS polymer in terms of the apparent volume of a flow unit. This is proceded by a discussion of the temperature dependence of the creep response. The subsequent sections consider the long-time response associated with viscous flow, and the stress dependence of the glass transition temperature.

Experimental Section

Apparatus. The creep apparatus shown in Figure 1 is a prototype of larger equipment now in construction, and has a temperature range from 40 to 100°, controlled to ±0.05°. The output of the displacement-indicating DCDT transducer is fed to a strip chart recorder from which data are read and subsequently processed and plotted by computer. (Further details are given elsewhere.[1])

The apparatus under construction will permit simultaneous measurements at five stress levels over a temperature range from −73 to 243°. Data will be obtained initially on a five-channel strip chart recorder although the apparatus will be compatible with analog-to-digital data acquisition systems.

Materials. The acrylonitrile–styrene–butadiene polymer has been described previously,[2] and corresponds to polymer I in ref 2.[3] It is a commercial polymer having the characteristics listed in Table I. Sheets of polymer were molded at 160° from which die-punched microtensile specimens (ASTM D 1708 configuration) were obtained.

Results

Temperature Dependence. Figure 2 shows a composite logarithmic plot of compliance, $D(t)$ [equal to strain divided by stress, $\epsilon(t)/\sigma$], *vs.* time at a stress of 0.91×10^8 dyn/cm^2 at seven temperatures. After the initial rapid increase in compliance at 50° a plateau region is observed which extends for about 2.8 decades. At later times a gradual increase in compliance is found which is probably associated with contributions from viscous flow processes as characterized by the steady-flow viscosity. Thus response characteristic of a noncross-linked polymer is observed at long times despite the fact that about one-third of the polymer is composed of cross-linked material. This response is not surprising in the absence of a continuous network, however, and undoubtedly the response includes contributions from slow retardation processes arising from slippage of entanglement junction points.

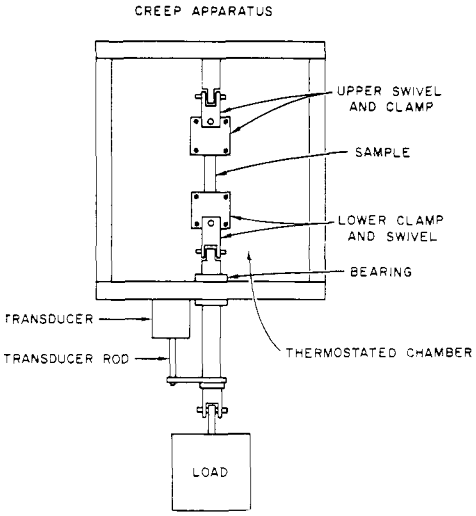

Figure 1. Diagram of tensile creep apparatus.

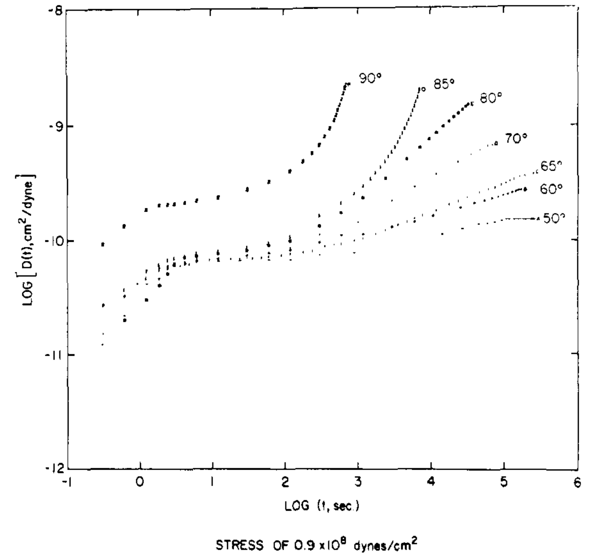

Figure 2. Logarithmic plot of creep compliance *vs.* time at a stress of 0.9×10^8 dyn/cm^2.

For times greater than about 100 sec, an increase in temperature results in a faster increase in compliance

---

(1) R. S. Moore and C. Gieniewski, *Polym. Eng. Sci.*, in press.
(2) B. D. Gesner, *J. Polym. Sci., Part A*, **3**, 3825 (1965).
(3) B. D. Gesner, private communication.

with time, which can be characterized by the decrease in steady-flow viscosity.

The length of the plateau region decreases with increasing temperature and is about 1 decade at 70°. The results from 80 to 90° indicate different time dependences than result at lower temperatures, and are associated with the complex response of the material near the glass transition temperature, T_g, of the styrene–acrylonitrile phase. This T_g is shown later to be close to 85°, the value found by dilatometry[4] for a closely similar polymer (polymer II of ref 2). The rapid increase in compliance at long times at 85 and 90° is particularly striking and is associated with response in rubbery flow. It is interesting that all curves superimpose vertically at short times except for that at 90°. This implies a rather small temperature dependence of compliance at short times at this stress level.

Similar results were obtained at nominal stresses of 1.75 and 0.60 × 10^8 dyn/cm.^{2} The effect of the higher stress could be observed, for example, in the rapid increase in compliance at 80°. At the lowest stress level the temperature dependence at short times was more pronounced than for either of the higher stress levels.

A general effect which occurs throughout these experiments is the lowering of T_g and, hence, a decrease of all relaxation times due to dilation in tensile elongation. This occurs because Poisson's ratio is about[5] 0.32 rather than 0.5 and upon deformation sample volume increases. The magnitude of the effect can be estimated by using the method of Ferry and Stratton[6] which involves the bulk compliance, rather than the thermal expansion coefficient as suggested by some workers.

Stress Dependence. The Model. Rather than analyzing the stress dependence of this ABS polymer by using empirical equations to describe the creep response, as in the work of Bergen,[5,7] it is felt that a more meaningful analysis can be obtained by considering the stress dependence in terms of a thermally activated rate process with a stress–sensitive energy barrier to flow. Such an approach comes under the general heading of Eyring rate theory, and although a similar procedure was used by Bueche[8] in describing creep in polystyrene, the experimental data and, hence, the analysis were rather limited.

Because analysis of the present data is the main object of this paper, the details of the model and its mathematical development will be minimized. The stress dependence of the compliance is considered to arise in part from the need to use a high level of stress in order to produce an appreciable rate of creep, and in part from the use of experimental test temperatures such that the thermal energy of the molecules in a flow unit is low relative to the amount of energy necessary to surmount the potential energy barrier associated with displacement to a new equilibrium position. If one considers a particular polymer segment and its motion in one dimension, the probability for motion in either direction in the absence of stress is equal. In the presence of stress the barrier to flow in the positive direction is lowered by virtue of the work done on the system while flow in the negative direction is further restricted. For relatively low temperatures the effect of stress on the energy barrier is sufficiently large to neglect effects associated with use of a one-dimensional model. This leads to a flow equation containing a sum of exponential terms. This equation can be stated in terms of a hyperbolic sine function as

$$v = K \sinh (f_0\delta/kT) \qquad (1)$$

where v is the velocity in units of strain per second and K is a parameter containing the activation energy to flow in the absence of stress. The quantity k is Boltzmann's constant, T is the absolute temperature, f_0 is the local applied force, and δ is the displacement required to reach the peak of the energy barrier. This equation has the prescribed functional form in that it leads to a linear dependence on stress (here designated as force) at low values of stress. From a plot of log K *vs.* $1/T$ it is possible in principle to obtain the activation energy for flow, ΔH_a. However, this approach turns out to be somewhat less satisfactory than other methods for describing the temperature dependence, as seen later.

TABLE II
VALUES FOR THE FLOW UNIT VOLUME[a] FROM EQUATION 2

T, °C	Time, sec 10^2	10^3	10^4	10^5
50	560	1440	738	1372
60	805	1266	1018	968
70	840	2370	(1395)[b]	
80			(2120)[b]	
85			(3710)[b]	

[a] In units of cubic ångströms. [b] Values uncertain.

As a first approximation the local applied force is taken as (A'/A) times the force on the specimen, where A' and A are the cross-sectional areas of the flow unit and the specimen, respectively. This leads to an expression for eq 1 in the form

$$v = K \sinh (\sigma V/kT) \qquad (2)$$

where σ is the tensile stress on the specimen and V corresponds to $A'\delta$. This has the dimensions of volume and should be similar in magnitude to the volume of a unit undergoing flow. It should be kept in mind that V is really the product of local displacement and local cross-sectional area, and that dilation at high temperatures as well as other effects can influence the magnitude of V. Thus interpretation of V as an actual flow unit volume should not be taken too literally.

The Apparent Volume of a Flow Unit. Values of creep velocity at constant temperature and the apparent volume of a flow unit were determined by the procedure outlined in the Appendix. The values so obtained for the apparent volume of a flow unit are listed in Table II. In general, they are in reasonable agreement with expectation being of the same order of magnitude as the size of a monomer unit. In particular, values obtained at the lower temperatures appear to show somewhat less variation and are considered more

---

(4) E. Scalco, T. W. Huseby, and L. L. Blyler, Jr., *J. Appl. Polym. Sci.*, **12**, 1343 (1968).

(5) R. L. Bergen, Jr., *SPE J.*, **23**, 57 (1967).

(6) J. D. Ferry and R. A. Stratton, *Kolloid Z.*, **171**, 107 (1960).

(7) R. L. Bergen, Jr., and W. E. Wolstenholme, *SPE J.*, **16**, 1235 (1960).

(8) F. Bueche, "Physical Properties of Polymers," Interscience Publishers, New York, N. Y., 1962, Chapter 11.

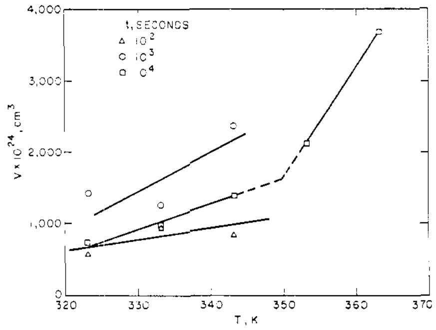

Figure 3. Plot of apparent flow unit volume *vs.* temperature for the times indicated.

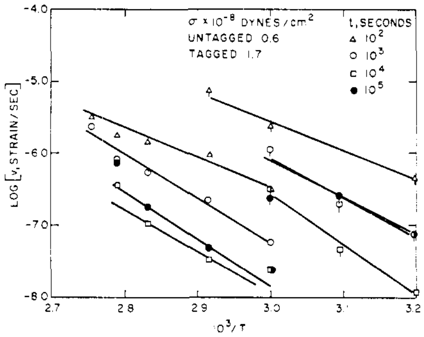

Figure 4. Plot of log v *vs.* $10^3/T$.

reliable. There appears to be some time dependence with a slightly larger value of V at longer times.

Plots of V *vs.* T are given in Figure 3. From the slopes of the lines values of the thermal expansion coefficient of V are obtained which range from 8 to 20 $\times$ 10^{-3}, 20–40 times the usual values found for polymers below T_g by dilatometry, etc. This is, perhaps, not too surprising in that V includes effects due to changes in δ with temperature so that the product $\delta A'$ would not necessarily have the same thermal expansion coefficient as the polymer. In part this may be an effect of the increase in compliance with temperature.

Values of K are given in Table III. In general, they show fairly consistent trends although they are not considered as reliable as the method discussed below for determining the temperature dependence, mainly due to the paucity of data at different stress levels for curve fitting. Plots of log K *vs.* $1/T$ give values for ΔH_a of 16.2, 25.8, 14.2, and 38.2 kcal/mol for values of log t equal to 2, 3, 4, and 5, respectively. Except for the value at 10^4 they indicate a consistent increase in ΔH_a with time, which is consistent with an increase in the apparent size of the flow unit.

TABLE III
VALUES FOR THE PARAMETER[a] K OF EQUATION 2

T, °C	Time, sec 10^2	10^3	10^4	10^5
50	1.86	0.022	0.063	0.021
60	2.89	0.213	0.127	0.14
70	8.34	0.144	(1.32)[b]	
80			(0.159)	
85			(0.098)	

[a] In units of 10^{-6} sec^{-1}. [b] Values in parentheses are rather uncertain.

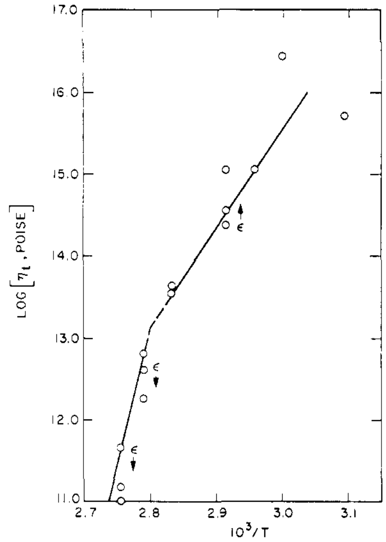

Figure 5. Graph of the logarithm of viscosity *vs.* $10^3/T$ as obtained from the data plotted in Figure 2.

In order to take advantage of the data at a number of temperatures at a single stress, plots of log v *vs.* $1/T$ were made as shown in Figure 4. At constant stress these plots give an effective activation energy which is to some extent biased by the applied stress. Results indicate that again ΔH_a increases slightly with time from about 19 to 29 kcal, although the change due to different stress levels is rather small. The latter is perhaps associated with the nature of fairly long-time response in that with a relatively small *net* activation energy at a low stress level the added stress does not change it significantly, *i.e.*, a relatively large number of molecules can surmount the barrier in both cases. This is not the behavior observed at short times, however, as discussed elsewhere.[1]

Response Governed by Viscous Flow. By looking at creep response at long times one has a means for determining the effective viscosity since it is this which determines the rate of creep after the region of steady flow has been obtained. In order to determine viscosity before this state has been reached at least four methods have been used which are summarized by Plazek[9] and which include the extrapolation procedure of Ninomya.[10] Since the main purpose of this section is to consider the temperature dependence of the tensile viscosity, η_t, the most frequently used method has been employed, in which the slope of a plot of D(t) *vs.* t at long times is taken as the reciprocal of the viscosity. In most cases data obtained at the longest times available were used except when the strain proved to be much greater than about 6%. The results are shown as a plot of log η_t *vs.* $10_3/T$ in Figure 5. A distinct break in the curve is found at about 84°, which is consistent with the value for T_g of the glassy matrix as obtained from short-time response.[1] It is also close to the "universal" value for the viscosity at T_g of about 10^{13} P.

It is clear from the data that two distinct and opposite effects of strain are observed on η_t depending on whether

---

(9) D. J. Plazek, *J. Phys. Chem.*, **69**, 3480 (1965).
(10) K. Ninomya, *ibid.*, **67**, 1152 (1963).

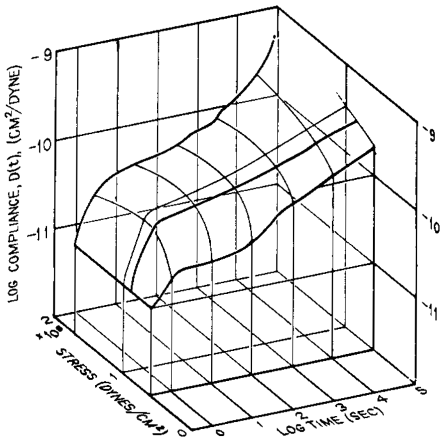

Figure 6. Projected three-dimensional plot of log compliance, stress, and log time for data obtained at 60°.

T is greater or less than T_g. Above T_g, η_t decreases with increasing strain, presumably because of dilational effects and the associated enhanced mobility as discussed earlier. Below T_g the magnitude of η_t increases with increasing ϵ. While this could be due to a time effect associated with approach to the true value of η_t, it could also indicate an increase in the actual value of the effective viscosity due to orientation of chains into the direction of stress at finite strains. (Studies of both creep and creep recovery could aid in distinguishing between the two cases.)

From the slopes of the curves in Figure 5 the activation energy is estimated to be 137 kcal/mol above T_g, and 55 kcal/mol below it. The former is close to the value obtained from the temperature dependence of the short-time response of compliance in the limit of zero stress,[1] 128 kcal/mol. This is reasonable since above T_g the over-all time dependence is much less and, hence, the apparent size of the flow unit should be essentially independent of time. Below T_g, the activation energy for η_t is larger than that obtained from either the short-time response,[1] the long-time response data of log K *vs.* $10^3/T$, or the long-time response data of log v *vs.* $10^3/T$, to which this type of measurement is closely similar. This is consistent with a larger time dependence and a greater size of the flow unit at longer times. It is clear from such results that below T_g a simple time–temperature superposition cannot be used over a large time scale because of the wide differences in activation energies.

An Alternative Representation of the Stress Dependence. In order to show the stress dependence of the logarithm of compliance as a function of the logarithm of time at a single temperature one can also use a three-dimensional plot as has been suggested by Andrews and Kazama[11] in studies on poly(vinyl chloride) films. An example of such a plot is given in Figure 6 for this ABS polymer at 60°. In principle, the stress required to produce a compliance curve with a particular, or characteristic slope at a given time is interpolated from a curve composed of points projected onto the stress–time plane. This stress is plotted as a function of temperature, as determined from similar plots at different temperatures, to estimate equivalent stress–temperature combinations for a particular isochrone. This approach requires one three-dimensional graph for each temperature, and a well-defined characteristic sharp increase in compliance over a short time interval.

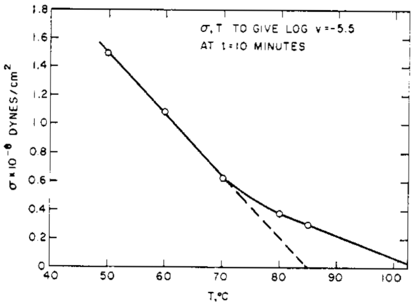

Figure 7. Stress–temperature combinations required to produce a velocity of creep of $10^{-5.5}$/sec at 10 min after loading.

An alternative approach to provide equivalent stress–temperature combinations for a particular creep velocity at 10 min after loading is given in the Appendix. The equivalent stress–temperature combinations determined in this manner are shown in a plot of σ *vs.* T in Figure 7. It is seen that an extrapolation of the low-temperature data gives a zero stress intercept of about 85°. (The calculated data in this temperature range indicate that a finite stress is still required although these data are rather uncertain.) In either case, one has a change in behavior near a characteristic temperature of about 85°, which is consistent with results from viscosity measurements, etc., although obtained in quite a different manner. Moreover, the results also clearly indicate the existence of the stress dependence of T_g.

Applications to Predictions of Creep Response. In considering the application of these results to estimates of dimensional stability of a polymer under load two restrictions must be kept in mind. First, the time–temperature superposition principle cannot be used over a larger time scale because of the wide differences in activation energies. Second, D(t) is a sensitive function of stress, even for relatively small deformations. Use of the rate-theory approach to predict D(t) at lower stress levels than those determined experimentally should produce reasonably good estimates but for values of σ higher than those measured experimentally the estimates may be too low due to enhanced flow caused by stress concentration and yielding, or, in the extreme case, by rapid failure. Use of a three-dimensional graph as in Figure 6 and the procedure associated with it should be valuable as an alternative means for obtaining estimates of creep response.

Conclusion

The stress dependence of creep in an ABS polymer was determined and analyzed in terms of a model in which the energy barrier to flow was lowered due to the work done by the applied stress. The result was stated in terms of the apparent volume of a flow unit, V, which was found to increase as either time and/or temperature increased. This was consistent with an increase in activation energy with time. The response at long times

---

(11) R. D. Andrews and Y. Kazama, *J. Appl. Phys.*, **38**, 4118 (1967).

was analyzed to determine the temperature dependence of the tensile viscosity. This was observed to be stress dependent and to increase with strain below T_g, and to decrease with strain above T_g probably because of dilational effects. In addition, the equivalent stress–temperature combinations to give a characteristic velocity 10 min after application of stress were determined. From the temperature dependence of the compliance, the temperature dependence of the viscosity, and the temperature at which the equivalent stress went to zero it was found that the effective glass transition temperature of the acrylonitrile–styrene phase is about 85° at low stress levels, but that it decreases with increasing stress. The activation energy was found to increase by a factor of at least 3 to 5 upon going from temperatures below T_g to values above it. This is consistent with a change in the apparent size of flow unit and with a marked change in the nature of the response. It was found that the time–temperature superposition principle could not be employed because of the use of test temperatures near and below the T_g of the glassy matrix. It was observed that the compliance was stress dependent partly because of the use of test temperatures such that the thermal energy of the molecules in a flow unit was low relative to the amount of energy necessary to overcome the barrier to movement to a new equilibrium position.

Acknowledgments. Discussions with Dr. S. Matsuoka regarding this work are gratefully acknowledged as are the suggestions of I. L. Hopkins regarding computer programming.

Appendix

Calculation of the Apparent Volume of a Flow Unit. In order to determine any effects of temperature or time on the apparent size of a flow unit, values of creep velocity were computed from isothermal plots of compliance *vs.* time at integer values of log t from 2 to 5. Attempts at fitting plots of log v *vs.* stress to values of the hyperbolic sine function proved cumbersome and so experimental plots of log v *vs.* log σ were superimposed on a master curve of log (v/K) *vs.* log $(\sigma V/kT)$ based on eq 2. The values of log $(1/K)$ and log (kT/V) were determined from the respective locations of the origins of the ordinate and the abscissa of the master curve on the experimental curve. (An alternative analysis for low temperatures in which flow in the negative direction is taken as zero would require $\sigma V/kT \gg 1$ in eq 2 so that this case is also considered by using the procedures described above.)

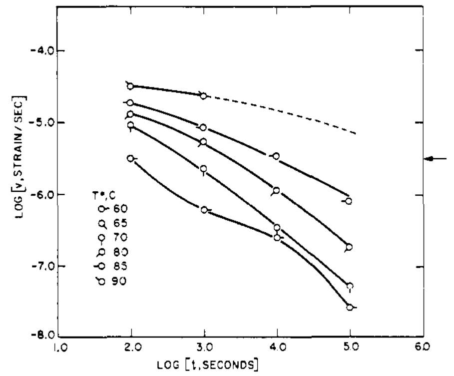

Figure 8. Logarithmic plot of velocity of creep *vs.* time at a stress of 0.6 × 10^8 dyn/cm^2 at the temperatures indicated.

Method for Determining Equivalent Stress–Temperature Combinations. In order to make use of the data of Figure 7, which lacks a well-defined sharp rise in log D, and to avoid plotting a series of three-dimensional graphs the following analysis using log v instead of log D was adopted. Logarithmic plots of v *vs.* t were made for each stress and temperature from the data already available, a typical example being given in Figure 8 for a stress of 0.6 × 10^8 dyn/cm.^{2} The time to reach a particular value of v was determined (in this case v equaled $10^{-5.5}$) and used as the abscissa in a plot of stress *vs.* log t at each temperature. From this plot the stress level for a particular isochrone (in this case 10 min) was determined and plotted as a function of temperature. Such a plot then provides the equivalent stress–temperature combinations necessary to produce a certain velocity of creep at 10 min after loading. This procedure is closely similar to that in which the slope of the log D *vs.* log t curve is used. Use of log v avoids any stress dependence and the analysis is a good approximation provided the ratio ϵ/t is constant or changes slowly over the range of measurements concerned. The time of 10 min although largely arbitrary was chosen since it corresponded to that used in the measurements of Andrews and Kazama. Reducing the time by about an order of magnitude would lower the zero stress intercept in Figure 7 by about 9° at 10^2 sec and raise it by 12° at 10^4 sec. This time dependence reflects in part the lack of a well-defined transition from which to choose a characteristic velocity and in part the inexact equivalence of using log v instead of log D and the associated variation of ϵ/t over the interval, as discussed above.