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Structural transition in poly(methyl methacrylate) due to large deformation at temperatures below the equilibrium second-order transition temperature

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To analyse the structural change in glassy polymers under large deformation at low temperatures, poly(methyl methacrylate) specimens were uniaxially compressed at temperatures below the equilibrium second-order transition temperature T_2 with varying strain rates. The state of steady plastic flow which appeared in the lower yield range of the stress–strain curve was analysed using the Eyring equation in a novel way. This analysis provided the following results: at low temperatures, the volume of a flow unit decreased with temperature, probably approaching the least critical value; and a functional relation between the activation enthalpy ΔH and the activation entropy ΔS for the glass deviated gradually from that for the melt derived from the WLF equation with decreasing temperature. This deviation could be attributed to the structural transition of the glass into liquid-like structures of the melt at elevated temperatures above $T_g + 100$ K where the WLF equation is no longer available.

1. Introduction

According to the physical definition of glass, the micro-Brownian motion of polymer chains should be limited in the glassy state. That is, to take an alternative conformation a molecular chain segment has to pass over an extremely high potential energy barrier. Thus it was formerly believed that the isothermal large deformation would be limited or impossible for glassy polymers. In practice, however, the plastic deformation of glassy polymers can easily be observed, and is often referred to as "cold drawing". To interpret this discrepancy, local adiabatic heating due to plastic work has been proposed [1]. However, this suggestion is now regarded as unlikely, as plastic deformation without rising temperature can be demonstrated by stretching or compressing a sample at very low deformation rates.

In the past two decades, several theories of isothermal structural changes due to imposed large strain have been introduced to explain the plasticity of polymer glasses. Robertson [2] proposed a transition of the glass into a liquid-like structure which can be induced by conformational changes due to imposed stress. Using the idea of a fictitious temperature introduced by Robertson, Rendell *et al.* [3] further developed their concept of a "coupling model of relaxation" to discusss the non-linear visco-elasticity. They could quantitatively predict the stress–strain relations of glassy polymers at constant and stepwisely changed rates of deformation, and also stress relaxations under large deformation. From the standpoint of the free volume, Shay and Caruthers [4] presented a theory of time-dependent structural change in glassy polymers. Contrary to these theories of rather homogeneous structural changes, Lefebvre and Escaig [5] related the amount of inhomogeneous defects induced by deformation with stress–strain relations and stress relaxations due to large deformation.

As experimental evidence for the structural change in glassy polymers, one of the authors (Y.N.) recently demonstrated a result verifying the transition of the glass into a liquid-like structure [6]. This result was deduced from the rate analysis of the steady plastic flow appearing in the lower yield range on stress–strain curves for poly(methyl methacrylate). A novel method of applying the Eyring equation to the steady plastic flow of the polymer glass provided a unique functional relation between the activation enthalpy ΔH and the activation entropy ΔS, which agreed with a functional relation between ΔH and ΔS derived from relaxation data for the melt of the same polymer. This agreement is direct evidence for the structural change of the glass into the melt structure. The agreement of these ΔH against ΔS functional relations indicates that the intermolecular interaction regulating the numerical values of ΔH and ΔS of the glass in the lower yield range is identical with that in the melt. Furthermore, this rate analysis contributes to ascertaining the physical significance of the Eyring factors obtained from the data of steady plastic flow in the polymer glass; these factors quantitatively represent the structural state of the flowing glass.

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Our experimental evidence for the structural change in glassy polymers has so far been obtained at relatively high temperatures below T_g, where the micro-Brownian motion of molecular segments is believed to be probable. It might therefore be suspected that the local segmental motion in the glass makes some contribution to the plastic deformation. Thus in the present study, the plastic deformation mechanism in poly(methyl methacrylate) (PMMA) is analysed in a temperature range below the equilibrium second-order transition temperature T_2 [7]. In this temperature range, the configurational change in the system is supposed to be completely prohibited as referred to the state of zero configurational entropy. This approach enables us to identify the plastic deformation mechanism in the lower temperature range with that in the higher temperature range; at temperatures below T_2, the structure of the glass is also changed into a liquid-like structure. The volume of a flow unit in the lower temperature range, however, becomes much smaller than that in the higher temperature range; the least size of the volume is found to be only ten times as much as the volume of a monomer unit. Extrapolation of this result into a further, lower temperature range leads to the suggestion that with decreasing temperature the volume of a flow unit approaches the least critical value, which is no longer dependent on temperature and strain rate.

2. Experimental procedure

Cylindrical specimens of 5 mm diameter and a height of 10 mm were cut from a commercial cast plate of PMMA, and followed by a heat treatment at 130 °C for 2 h. The glass transition temperature T_g and the WLF parameters c_1^g and c_2^g for this PMMA sample were evaluated from relaxation data as follows [6]

$$T_g = 389\ \text{K}$$

and

$$c_1^g = 21.1 \quad \text{and} \quad c_2^g = 66.4$$

The cylindrical specimens were uniaxially compressed at various constant deformation rates using an electro-hydraulic servocontrolled machine. In a temperature-controlling cabinet, the temperature of specimen was regulated at required temperatures within a deviation of 1 K in a range from + 60 to − 60 °C. Each side of a specimen was directly in contact with a mirror-like surface of steel compression discs without lubricant.

3. Results and discussion

3.1. Compression stress–strain curves

The transition temperature T_2 of the PMMA sample could be predicted as

$$T_2 = T_g - c_2^g = 323\ \text{K}\ (50\ ^\circ\text{C})$$

Fig. 1 shows true stress against nominal strain (σ_t against ε_n) curves obtained at variations of temperature ranging from T_2 to 223 K (− 50 °C) at a constant compression strain rate of $3.13 \times 10^{-5}\ \text{sec}^{-1}$.

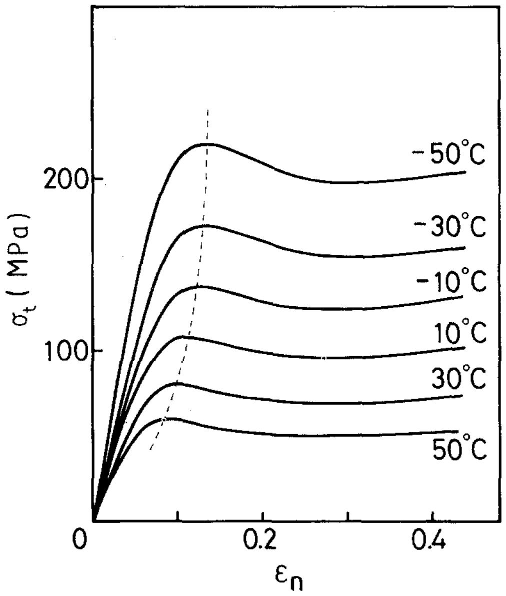

Figure 1 Compression stress–strain curves for PMMA at temperatures below the equilibrium second-order transition temperature T_2(50 °C). $\dot{\varepsilon}_n = 3.13 \times 10^{-5}\ \text{sec}^{-1}$.

The true stress σ_t was calculated on an assumption of uniform deformation and isovolume of specimen during the uniaxial compression.

As indicated by a dashed line in Fig. 1, the strain at the yield point approached to a constant value ($\sim$ 0.13) with decreasing temperature. A similar result has been presented by Lefevbre *et al.* [8] for PMMA by compression tests at low temperatures. The temperature-dependence of yield strain will be discussed later in terms of the structural change in the yield process.

Passing through the yield point, the true stress then decreased to the minimum value in a post-yield plateau range, which will be referred to as lower yield range. As indicated in a previous paper [6], this lower yield range can reasonably be considered as a state of steady plastic flow in the glassy polymer. Because of the steadiness of the flow, the Eyring equation can convincingly be applied to the lower yield state to analyse the plastic flow as a rate process in molecular terms.

3.2. Rate-process analysis of plastic flow in the lower yield range

The Eyring equation for plastic flow under a uniaxial stress σ at a constant strain rate $\dot{\varepsilon}$ is given by the expression

$$\frac{\sigma}{T} = \frac{9.212\,k}{v_a}\left(\log\dot{\varepsilon} - \log CT + 0.4343\frac{\Delta H}{RT}\right) \quad (1)$$

where v_a is the apparent shear activation volume; ΔH is the activation enthalpy; and C is a factor including activation entropy ΔS in the form

$$C = \left(\frac{2\lambda k}{3\lambda_1 h}\right)\exp\left(\frac{\Delta S}{R}\right) \quad (2)$$

The quantities λ and λ_1 in Equation 2 represent the distances between two neighbouring flow units in vertical and parallel directions to a shear-flow plane, respectively. Equation 1 predicts a linear functional relation between σ/T and $\log\dot{\varepsilon}$ if the Eyring factors ΔH, v_a and C are of constant values, i.e. if the structure of the flowing system remains unchangeable at varying of strain rates.

Experimental data for the lower yield stress σ_l divided by temperature T in a temperature range from -60 to $+60\,^\circ$C are plotted against $\log\dot{\varepsilon}$ in Fig. 2. Temperature rise during plastic flow was seen as shown, for instance, for the case of $-30\,^\circ$C. As indicated by a dashed line drawn through the experimental points at $-30\,^\circ$C, with increasing strain rate the quantity σ_l/T reached the maximum value, and thereafter decreased continuously. This is attributable to a rise in specimen temperature caused by insufficient dispersion of the heat generated by plastic work, which was achieved in a relatively short time at higher strain rates. It was also observed that the strain rate at which the quantity σ_l/T showed the maximum value decreased with temperature. This is due to the fact that with decreasing temperature, the specific heat of the sample decreases while the amount of plastic work increases. Thus, to analyse the flow in the glass at constant temperatures, the experimental points which were apparently influenced by temperature rise in specimens, as shown for $-30\,^\circ$C, are excluded from Fig. 2 for other temperatures. After this exclusion, the experimental points at each temperature in a lower strain-rate range, where the effect of the temperature rise was ignored, could be represented by a curve with a slope increasing gradually with $\log\dot{\varepsilon}$. As illustrated in the previous paper [6], these curves can be analysed using the Eyring equation in a novel way: a curve is approximated by successive line elements with different slopes, and parallel line elements at different temperatures represented by Equation 1 are determined so as to give the best fit to the data. Sets of parallel line elements labelled by alphabetical marks *a* to *k* in Fig. 2 were obtained in this way, and the corresponding numerical values of the Eyring factors ΔH, v_a and C are summarized in Table I.

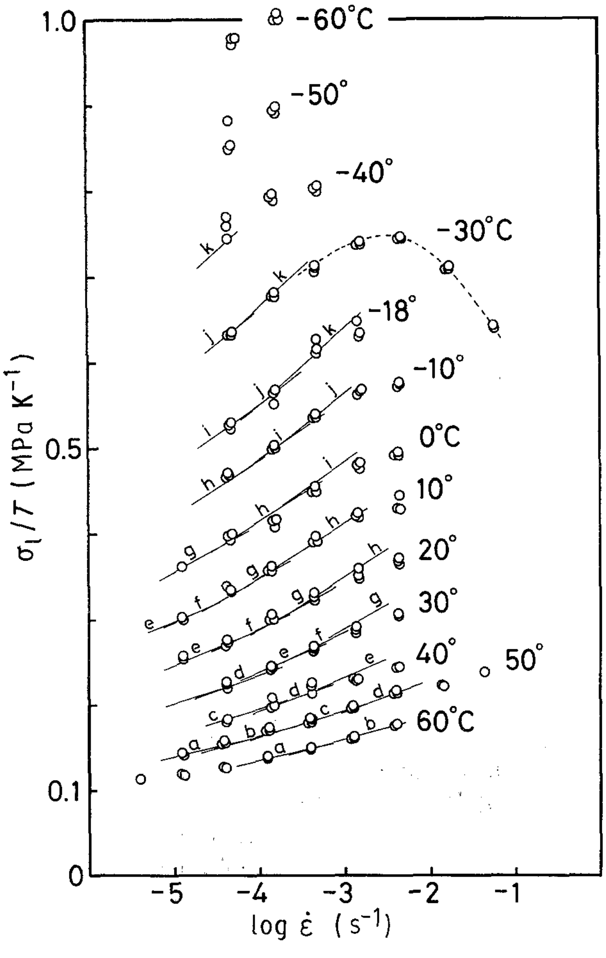

Figure 2 The ratio of lower yield stress σ_l divided by temperature T plotted against the logarithm of true strain rate $\dot{\varepsilon}$.

Assuming that the distances λ and λ_1 are equivalent, we have from Equation 2

$$\Delta S = 19.15\,(\log C - 10.14)\ (\mathrm{J\,mol^{-1}\,K^{-1}}) \qquad (3)$$

This expression provides experimental values of the activation entropy for the plastic flow in the glassy polymer. Hence the quantity ΔS, and also ΔH, obtained from the glass will hereafter be denoted using a superscript (g). Substitution of $\log C$ (given in Table I) into Equation 3 thus enables us to show a functional relation between $\Delta S^{(g)}$ and $\Delta H^{(g)}$.

For the state of melt, a functional relation between the activation entropy, $\Delta S^{(m)}$, and the activation enthalpy, $\Delta H^{(m)}$, is derived from the WLF equation as [6]

$$\sqrt{\Delta H^{(m)}} = \sqrt{T_g - c_2^g}\,\sqrt{\Delta S^{(m)}} + \sqrt{2.303\,R c_1^g c_2^g} \qquad (4)$$

where a superscript (m) refers to the melt. This expression represents a linear function between $(\Delta H^{(m)})^{1/2}$ and $(\Delta S^{(m)})^{1/2}$ with a slope of $(T_g - c_2^g)^{1/2}$ intersecting the axis of $(\Delta H^{(m)})^{1/2}$ at a point $(2.303\,Rc_1^g c_2^g)^{1/2}$. Since the glass transition temperature T_g and the parameters c_1^g and c_2^g for the PMMA sample have been determined from relaxation data as $T_g = 389$ K, $c_1^g = 21.2$ and $c_2^g = 66.4$, substitution of these values into Equation 4 gives

$$\sqrt{\Delta H^{(m)}} = 17.96\sqrt{\Delta S^{(m)}} + 5.19 \qquad (5)$$

As discussed previously [6], numerical values of ΔH and ΔS represent quantitatively the effect of intermolecular interaction on the displacement of polymer chains. In other words, the values of ΔH and ΔS can be uniquely related to the structure of a flowing polymeric system, because the structure of the system is

TABLE I Eyring factors obtained by fitting Equation 1 to data shown in Fig. 2

Label	ΔH (kJ mol^{-1})	v_a (nm^3)	$\log C$
a	276.3	5.30	31.21
b	247.0	4.54	27.56
c	226.0	3.97	24.97
d	209.3	3.53	22.91
e	194.6	3.03	21.37
f	180.0	2.65	19.59
g	163.2	2.27	17.47
h	150.7	1.86	15.91
i	142.3	1.82	14.88
j	131.9	1.59	13.68
k	125.6	1.41	13.19

determined in principle by the intermolecular interaction. Accordingly, the comparison of the functional relation between $\Delta H^{(g)}$ and $\Delta S^{(g)}$ with Equation 5 is probably to provide experimental evidence on the structural change of the glass into a liquid-like structure. In Fig. 3, the functional relation of $(\Delta H^{(g)})^{1/2}$ to $(\Delta S^{(g)})^{1/2}$ is compared with Equation 5. It is seen that the experimental points in each temperature range fall on a single continuous curve. As stated previously, the experimental points for the glass in the higher temperature range were in good agreement with Equation 5. This agreement verifies the transition of the glass into a liquid-like structure at higher temperatures. In the lower temperature range, however, the experimental points deviate gradually from the straight line of Equation 5.

A likely explanation is that Equation 5, in the region where the deviation occurs, corresponds to an expression of the WLF equation extrapolated into a much higher temperature range where this empirical equation is no longer available for the temperature dependence of relaxation. With respect to the temperature range available for the WLF equation, it has been believed that the range from T_g to nearly $T_g + 100$ K is acceptable, and at higher temperatures the relaxation processes are governed by more specific features [9]. Thus if the structure of the glass is changed into a liquid-like structure for the melt at higher temperatures beyond this temperature range, the relation between ΔH and ΔS for the liquid-like structure can no longer be compared with the corresponding functional relation from the WLF equation. To give a coordinate of structural temperature to Fig. 3, therefore, the quantity ΔS on the abscissa was converted to a corresponding temperature T of the melt through the following equation:

$$\Delta S = \frac{2.303\, R c_1^g c_2^g \,(T_g - c_2^g)}{(T - T_g + c_2^g)^2} \qquad (6)$$

This calculation gives a second abscissa, $T - T_g$, as shown in Fig. 3. It is noticeable that the experimental points of $\Delta H^{(g)}$ against $\Delta S^{(g)}$ begin to deviate from Equation 5 nearly at $T - T_g = 100$ K. Accordingly, it is presumed that the functional relation of $\Delta H^{(g)}$ against $\Delta S^{(g)}$ in the lower temperature range rather represents a relation of $\Delta H^{(m)}$ to $\Delta S^{(m)}$ for the melt at temperatures higher than $T_g + 100$ K, and the structure of the glass has made a transition into that for the melt at the higher temperatures. In consequence, the comparison between the functional relations of $\Delta H^{(g)}$ against $\Delta S^{(g)}$ and $\Delta H^{(m)}$ against $\Delta S^{(m)}$ illustrated in Fig. 3 has led to the suggestion that, when imposed by large strain at very low temperatures, the glass was changed into a liquid-like structure of the melt at very high temperatures.

Furthermore, data of the viscosity for the PMMA melt will provide further confirmation of this glass-to-liquid transition. Comparable viscosity data for the cast-moulding PMMA sample has not been presented, as the sample suffers thermal resolution at elevated temperatures because of its high molecular weight. For an injection-moulding PMMA sample of moderate molecular weight, however, Asami [10] has presented the viscosity data as a function of temperature and strain rate over a temperature range from 200 to 260 °C. Derived from his data, the experimental functional relation between the zero-shear viscosity η_0 and temperature T for the injection PMMA sample is represented by the following Arrhenius-type equation:

$$\eta_0 = A \exp\left(\frac{\Delta H^{(m)}}{RT}\right) \qquad (7)$$

where

$$\Delta H^{(m)} = 146.5 \ (\text{kJ mol}^{-1})$$

and

$$\ln A = -27.21$$

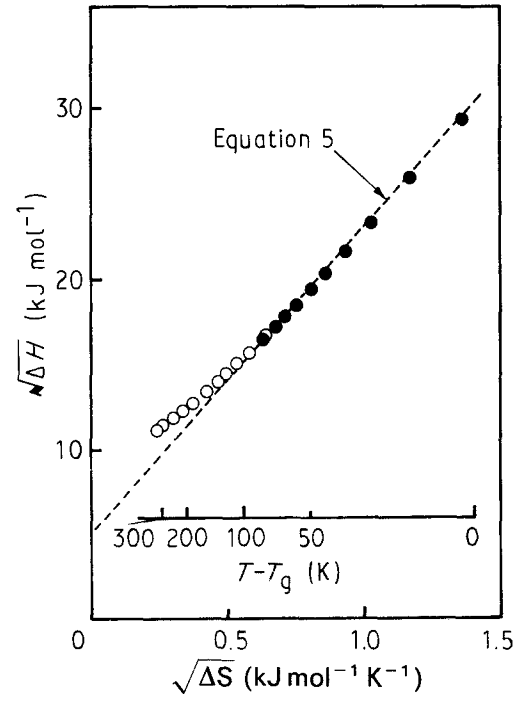

Figure 3 An experimental functional relation of $(\Delta H)^{1/2}$ against $(\Delta S)^{1/2}$ for the steady plastic flow compared with Equation 5 for the relaxation in the melt. ○, data obtained at lower temperatures in this work; ●, previously reported data obtained at higher temperatures [6].

The zero-shear viscosity equation for the liquid-like structure of the PMMA glass can be predicted in the following way: the unapproximated original form of Equation 1 is given by [11, 12]

$$\dot{\gamma} = \left(\frac{2\lambda k}{\lambda_1 h}\right) T \exp\left(-\frac{\Delta H + p v_p}{RT}\right) \exp\left(\frac{\Delta S}{R}\right) \sinh\left(\frac{\tau v_s}{2kT}\right) \qquad (8)$$

This equation holds for a liquid-like structure which is uniquely defined by numerical values of ΔH, ΔS, v_s and v_p. If we suppose this liquid-like structure to flow under very low stress, τ, without changing its structure (i.e. without changing the values of ΔH, ΔS and v_s), then an equivalent to the zero-shear viscosity for this structure can be reduced from Equation 8 as

$$\eta_0' = \lim_{\substack{\tau \to 0 \\ p \to 0}} \frac{\tau}{\dot{\gamma}} = \frac{\lambda_1 h}{\lambda v_s} \exp\left(-\frac{\Delta S}{R}\right) \exp\left(\frac{\Delta H}{RT}\right) \qquad (9)$$

In this expression v_s denotes shear activation volume, which has experimentally been shown to be related to the apparent activation volume v_a evaluated under uniaxial compressive stress in the form [13]

$$v_a = 1.08\, v_s \tag{10}$$

Consequently, using experimentally evaluated parameters v_a, C and $\Delta H^{(g)}$, Equation 9 is expressed as

$$\eta_0' = A' \exp\left(\frac{\Delta H^{(g)}}{RT}\right) \tag{11}$$

where

$$A' = \frac{0.72\, k}{C v_a} \tag{12}$$

Now we compare the experimental relation of $\ln A'$ against $\Delta H^{(g)}$ with the point of $\ln A$ against $\Delta H^{(m)}$ from Asami's data. The result is shown in Fig. 4. The experimental point of $\ln A$ against $\Delta H^{(m)}$ falls right on a straight line drawn through the data of $\ln A'$ against $\Delta H^{(g)}$. This agreement convincingly indicates the transition of the glass into liquid-like structures of the melt at high temperatures. In consequence, it is concluded that during the plastic deformation at low temperatures, the glass changes its structure into a liquid-like melt structure at high temperatures.

Another significant Eyring parameter obtained by the rate analysis is the apparent shear activation volume, v_a. In Fig. 5, the activation enthalpy $\Delta H^{(g)}$ is plotted against the activation volume v_a. With decreasing temperature, $\Delta H^{(g)}$ decreased linearly with v_a. Another ordinate, n, representing the number of monomer units in an activation volume, provided a linear function between $\Delta H^{(g)}$ and n, showing a inclination of 5.13 kJ mol^{-1} per monomer unit. This inclination means $\Delta H^{(g)}$ increased by 5.13 kJ mol^{-1} for each additional increment of a monomer unit to the activation volume.

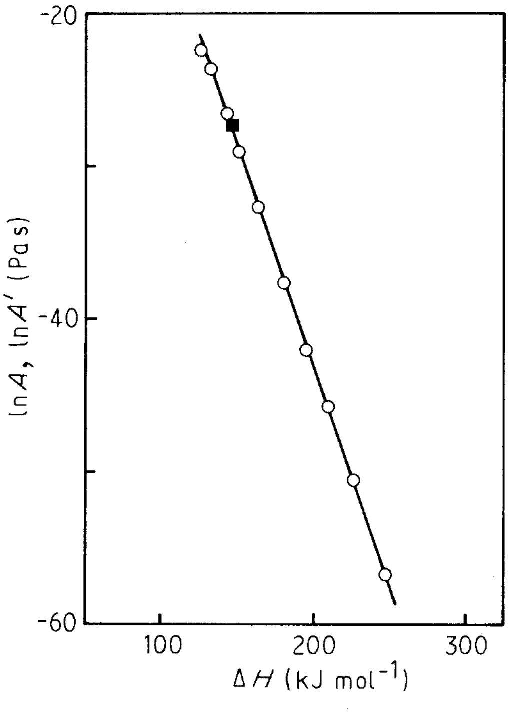

Figure 4 Functional relation between zero-shear viscosity factors for the liquid-like structure of PMMA, showing an excellent agreement with that for the melt. ○, Glass; ■, Melt.

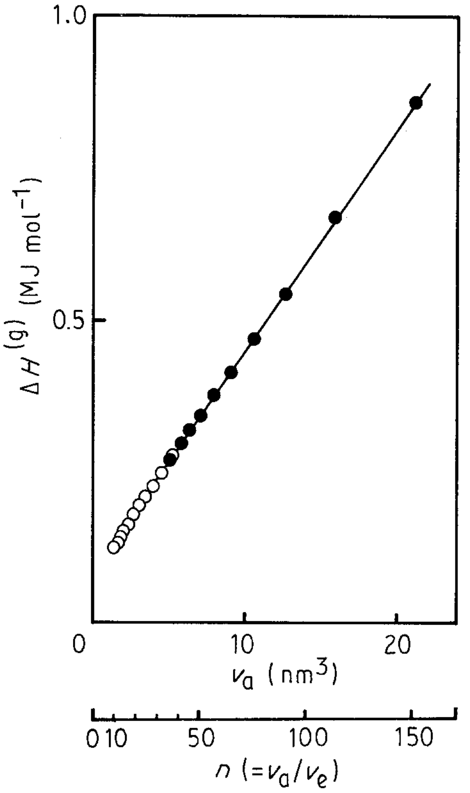

Figure 5 A linear relation between the activation enthalpy $\Delta H^{(g)}$ and the activation volume v_a or the number of monomer units n in v_a. ○, data obtained at lower temperatures in this work; ●, previously reported data obtained at higher temperatures [6].

As presented in Table I, the minimum value for v_a obtained in this work was 1.41 nm^3. This is equivalent to a volume of only about 10 monomer units, and is far less than that obtained at higher temperatures near T_g (e.g. 100 to 150 monomer units [6]). This result leads to the question, what is the least size for v_a? Thus the quantity v_a was plotted against temperature T in Fig. 6 at variations of $\log \dot{\varepsilon}$. It is seen that v_a ap-

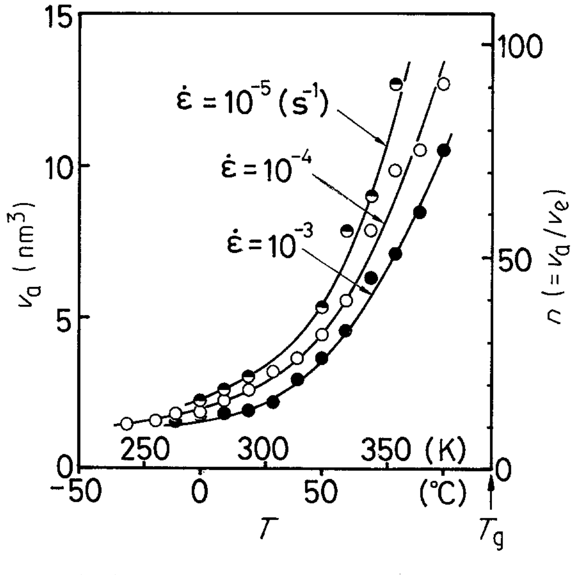

Figure 6 A plot of the activation volume v_a or the number of monomer units, n, in v_a against temperature T at varying strain rates, exhibiting the least critical size for v_a at lower temperatures.

proaches a certain finite value with decreasing temperature. This can reasonably be expected as an independent cooperative movement of monomer units without accompanying adjacent monomers would be impossible if n decreased as low as two or three. Thus the independent cooperative movement is likely only for rearranging monomer units, the number of which is larger than a certain limited value. This should be the least size of the activation volume, which will be denoted as v_a^*. Hence each curve in Fig. 6 is supposedly approaching v_a^* with decreasing temperature (the critical volume v_a^* for the PMMA sample may be estimated to be at least several times as large as that of a monomer unit). With further decreasing temperature, then, v_a will reach or become nearly equal to v_a^*, which is necessarily independent of temperature and strain rate. In this critical situation, $\Delta H^{(g)}$ and $\Delta S^{(g)}$ will also approach the critical values ΔH^* and ΔS^*, respectively, corresponding to the ultimate size v_a^*. Thus the plastic flow for this state is expected to be reproduced by a single Eyring equation of a form

$$\frac{\sigma}{T} = \frac{9.212\,k}{v_a^*}\left(\log\dot{\varepsilon} - \log C^*\,T + 0.4343\,\frac{\Delta H^*}{RT}\right) \tag{13}$$

where

$$C^* = \left(\frac{2\lambda^* k}{3\lambda_1^* h}\right)\exp\left(\frac{\Delta S^*}{R}\right) \tag{14}$$

It should be noticed that the gradual approach of $\Delta H^{(g)}$ to the critical constant value ΔH^* in the glass with decreasing temperature is symmetrical to the behaviour of $\Delta H^{(m)}$ for the flow of the melt: the quantity $\Delta H^{(m)}$ approaches a constant value with increasing temperature, and at high temperatures the viscosity of the melt can frequently be approximated by the Arrhenius equation with a temperature-independent value of activation enthalpy. This is illustrated in Fig. 7. The experimental points are the data of the activation enthalpy $\Delta H^{(g)}$ plotted against temperature, T, whereas the solid curve is a functional relation between $\Delta H^{(m)}$ and T for the melt deduced from the relaxation data. A dashed line is a mirror image of the solid curve reflected by a fictitious mirror placed at T_g, showing a good agreement with the data from the glass. This symmetrical behaviour of ΔH with respect to T_g is understood as a result of the structural transition of the glass – with decreasing temperature the liquid-like structure of the glass shifts to that of the melt at higher temperatures.

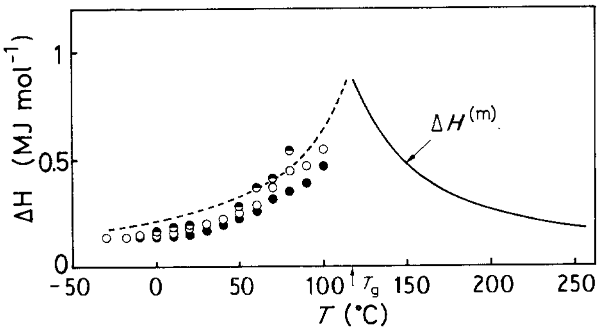

Figure 7 Symmetrical relation of $\Delta H^{(g)}$ and $\Delta H^{(m)}$ with respect to the glass transition temperature T_g. $\dot{\varepsilon}$ = ◒, 10^{-5}; ○, 10^{-4}; ●, 10^{-3} sec^{-1}.

3.3. Transition mechanism in the solid polymer from glassy to liquid-like structure at temperatures below T_2

As illustrated in the previous paper, the yielding of the glassy polymer can be understood as a transient phenomenon, resulting from a strain-induced decrease of the volume of the cooperatively rearranging region to the least size in the lower yield range. Thus the yield point has been concluded to be an unstable state of flow, revealed only instantaneously in this transient state. The aim of this final section is to discuss the effect of the size of activation volume on yield strain ε_y (strain at the yield point), and the strain range in the lower yield state.

A comparison of the temperature dependence of ε_y (shown in Fig. 1) with the relation of v_a to temperature (shown in Fig. 6) leads us to find a close relationship between ε_y and v_a; with decreasing temperature, ε_y increased to reach the maximum constant value as indicated by the dashed line in Fig. 1, while v_a decreased towards the least critical size v_a^*. A similar relation was observed between ε_y and v_a when compression tests were conducted at varying strain rates at a constant temperature; ε_y increased with strain rate whereas v_a decreased. Further, it is seen that the strain range of the lower yield state shifted to higher values with decreasing temperature (see Fig. 1) or increasing strain rate, although the quantitative amount of the shift was not obvious because of the considerable flatness of the plateau range. Thus, from these temperature and strain-rate dependences of v_a, ε_y and the strain range of the lower yield state, it can be shown that with decreasing size of v_a in the lower yield state, both the strains at the yield point and in the lower yield range increase. This implies that more strains are required for passing through the yield point and reaching the lower yield state with lessening activation volume. As discussed above, however, the size of decreasing activation volume is presumably limited to the critical volume v_a^*. Thus at this limited stage both the yield strain and the strain range in the lower yield state are supposed to become temperature and strain-rate independent.

4. Conclusions

The rate analysis of the steady plastic flow at low temperatures for PMMA provided the following results:

1. Large strains induced the structural change of the glass into liquid-like structures when imposed at temperatures below T_2, as well as at higher temperatures.
2. With decreasing temperature of the glass, its liquid-like structure shifted to that of the melt at more elevated temperatures.
3. The quantities ΔH and v_a for the liquid-like structure approached their respective critical values

with decreasing temperature. Thus a critical state of the liquid-like structure was expected to exist for the structural transition at very low temperatures.

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